hydroquinone is a reducing agent and dihydroxymaleic acid possesses a double bond, it is quite reasonable to suppose that the acid is reduced to tartaric. That such is the case is shown in the last table, in which tartaric acid was used in such a concentration as would result when 0.0376 g. of dihydroxymaleic acid is reduced at the ethylene linkage.

Moreover, assuming that each gram molecule of quinhydrone contributes 2 g. of hydrogen, 0.08 g. would provide 0.00073347 g. of hydrogen; 0.0376 g. of dihydroxymaleic acid requires 0.0004087 g. of hydrogen and constant readings should be obtained using this amount; 0.06 g. would supply 0.0004396 g. of hydrogen for the reduction of the acid and the remaining 0.02 g. produces the pressure of hydrogen ions at the electrode.

Pirie and Pinhey[4] have observed that glutathione, a substance well known to be very easily oxidized and reduced, has a similar effect in upsetting the quinone–hydroquinone equilibrium. Dihydroxymaleic acid, therefore, may be compared to glutathione with respect to the ease with which it may be reduced.

Conclusion

It is shown above that the quinhydrone electrode is not applicable to all unsaturated acids.

From the standpoint of a study of this acid, the results are doubly interesting since they indicate the reactivity of this double bond, heavily laden as it is with highly negative groups.

MONTREAL, CANADA

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF JOHNS HOPKINS UNIVERSITY]

PREPARATION OF SOME CYCLOPENTANE DERIVATIVES

BY W. R. EDWARDS, JR.,[1] AND E. EMMET REID

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Alicyclic compounds are known to be present in many crude petroleums as well as in a variety of other natural substances. When their diversity and the number of their theoretically possible modifications are considered, our knowledge of them seems relatively meager. In the present work a study has been made of the reactions between cyclopentylmagnesium halides and a variety of aldehydes. Previous employment of the former in the Grignard reaction has been confined to a very few instances, cyclopentylsulfonic acid,[2] cyclopentylcarboxylic acid,[3] cyclopentyl carbinol[3,4] and γ-cyclopentylpropanol[5] having been made thereby.

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[4] Pirie and Pinhey, *J. Biol. Chem.*, **74**, 323 (1929).

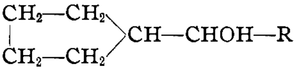
[1] From the Ph.D. dissertation of W. R. Edwards, Jr., 1928.

[2] Borsche and Lange, *Ber.*, **40**, 2220 (1907).

[3] Zelinsky, *ibid.*, **41**, 2627 (1908).

[4] Wood and Scarf, *J. Soc. Chem. Ind.*, **42**, 13T (1923).

[5] Adams and Noller, THIS JOURNAL, **48**, 1080 (1926).

We have obtained and characterized a new series of secondary alcohols of the type  $\begin{matrix} CH_2\text{—}CH_2 \\ | \\ CH_2\text{—}CH_2 \end{matrix} \rangle CH\text{—}CHOH\text{—}R$ where "R" represents the following radicals: methyl, ethyl, *n*-propyl, *n*-butyl, *n*-hexyl and phenyl. An attempt to obtain the anisyl derivative was unsuccessful owing to the pronounced decomposition of the product on distillation. For characterization, crystalline derivatives of these carbinols have been prepared.

As the starting point for these syntheses, cyclopentanone was made from commercial cyclohexanol by standard methods and reduced both by standard methods and by the method of Wislicenus and Hentzschel[6] and by the catalytic method of Adams and his co-workers,[7] to cyclopentanol. Certain modifications tending toward better yields or greater convenience and rapidity were introduced into these processes. Both the bromide and the chloride were prepared from cyclopentanol and employed in the earlier part of the work; but as the bromide proved more satisfactory, it was used exclusively for the later preparations. The magnesium complex usually formed readily and reacted smoothly with the aldehydes. The resulting carbinols are high-boiling liquids, and received their final purification by fractionation at reduced pressures. The alkyl derivatives showed no signs of decomposition during distillation; but the phenyl derivative was slightly affected, and the anisyl product was very largely decomposed.

Table I gives a number of the constants of these compounds. The five alkyl cyclopentyl carbinols exhibit fairly regular elevation in boiling point and decrease in density as the number of carbon atoms increases. Since

TABLE I

DATA ON COMPOUNDS

Compound C_5H_9CHOHR R =	Boiling points				Densities		Refr. index	Mol. refr. $[(n-1)M]/d$	Melting points, °C. (corr.)			Analysis			
	Press., mm.	Temp., °C. (corr.)	Press., mm.	Temp., °C. (corr.)	25°/4°	0°/4°			3,5-dinitro benzoate	Phenyl-urethan	α-Naphthyl urethan	Found C	Found H	Calcd. C	Calcd. H
Methyl	31–32	73.5–75	52.5	85–85.5	0.9163	0.9342	1.45 1	56.55	86	71–71.5°	104	73.46	12.29	73.61	12.37
Ethyl	18	72.5–74.5	52.5	97.5–98.5	.9035	.9219	1.4502	63.84	83.5	Oil	91	74.77	12.48	74.92	12.59
n-Propyl	..	...	52	114.5–115.5	.8970	.9146	1.4510	71.46	85	Oil	85	75.79	12.75	75.98	12.76
n-Butyl	23	114–115			.8935	.9115	1.4548	79.48	63.5	Oil	..	76.51	12.80	76.85	12.91
n-Hexyl	12–12.5	129.5–130.5			.8848	.9012	1.4562	94.97	Oil	Oil	Oil	77.88	12.96	78.19	13.13
Phenyl	5	129–131			1.0346	1.0531	....	...	Oil	Oil	..	80.96	8.51	81.76	9.16

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[6] Wislicenus and Hentzschel, *Ann.*, **275,** 322 (1893).

[7] Adams and Noller, Ref. 5, and earlier work by Adams and co-workers.

this work was done Bedos[8] has prepared the methylcyclopentyl carbinol in an entirely different way. He gives the melting point of the phenylurethan as 70–71°.

In general, the by-products of the Grignard reactions were not examined; but one unexpected secondary reaction was noted and studied. During the reaction between benzaldehyde and cyclopentylmagnesium bromide, a small quantity of a substance identified as 1,3-dibenzylidene-cyclopentanone-2 was formed. It was first observed after the Grignard complex had been decomposed with dilute hydrochloric acid; after standing overnight, yellow needles of the compound, which is only slightly soluble in cold ether, were observed. The attempt to prepare anisylcyclopentyl carbinol was made in order to determine whether or not a similar secondary reaction would take place. Crystals appeared in the same manner, and were identified as 1,3-di-*p*-methoxybenzylidene-cyclopentanone-2, the condensation product of anisic aldehyde with cyclopentanone.

Compounds of this type are readily formed[9] by condensation of one molecule of cyclopentanone with two molecules of an aromatic aldehyde, under the influence of certain condensing agents, of which hydrochloric acid is one. One of the possible explanations of this occurrence is that the cyclopentyl bromide employed in the reaction retained a small amount of cyclopentanone, that this cyclopentanone in some manner resisted the normal tendency to unite with the cyclopentylmagnesium bromide as soon as the latter was formed, and that it did react with a portion of the benzaldehyde, under the influence of the hydrochloric acid, following the addition of the latter. Steric hindrance might account for its failure to form completely a complex with cyclopentylmagnesium bromide, or for its displacement from such a complex by benzaldehyde. It is of interest to note that Sabatier and Mailhe[10] working with the analogous cyclohexyl compounds, succeeded in forming 1,1-cyclohexylcyclohexanol from cyclohexylmagnesium chloride and cyclohexanone; but that they report that there is much secondary action, and that the yield "is not very good." The quantity of cyclopentanone which would have had to be present to account for the quantity of crystals formed would be equivalent to a little more than 1% of the quantity of cyclopentyl bromide. The latter was actually found to contain a trace of the ketone.

To test this theory, a further experiment was made, using the cheaper cyclohexyl compounds, in the belief that they would behave sufficiently like their cyclopentyl prototypes. Cyclohexyl chloride was prepared and divided into two portions, A and B. A small portion of cyclohexanone was added to A, while B was subjected to a careful treatment designed to

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[8] Bedos, *Compt. rend.*, **189**, 255 (1929).

[9] Vörlander and Hobohm, *Ber.*, **29**, 1840 (1896).

[10] Sabatier and Mailhe, *Ann. chim. phys.*, [8] **10**, 547 (1907).

remove any trace of ketone. Each portion was then used to form cyclohexylmagnesium chloride, which was treated in the usual manner with benzaldehyde, followed by hydrochloric acid. From the reaction employing portion A, a fair quantity of 1,3-dibenzylidene-cyclohexanone-2 was obtained; but no trace of this compound could be found in the products of the reaction employing portion B. The result of this experiment strengthens the above explanation.

A further experiment, in which cyclohexyl chloride containing cyclohexanone was used, and a very slight excess of dilute acetic acid substituted for hydrochloric acid as the neutralizing agent, failed to yield any of the condensation product, establishing the hydrochloric acid as the condensing agent.

Experimental

Preparation of Adipic Acid.—This was prepared from commercial cyclohexanol, by oxidation with boiling concentrated nitric acid, employing the method described in "Organic Syntheses."[11] Stirring proved unnecessary, since active boiling with a sufficient excess of the acid ensured rapid and complete conversion. By using a five-liter balloon flask containing 2 liters of nitric acid, it was possible to convert 625 g. of cyclohexanol in a single run. After washing with 100 cc. of cold 1:3 nitric acid, followed by 150 cc. of ice water, and air-drying on a porous plate, the adipic acid crystals were nearly white, and suitable for further use; yield, 55%.

Preparation of Cyclopentanone.—The method described in "Organic Syntheses"[11] was followed.

Preparation of Cyclopentanol.—(1) With sodium and moist ether, by the method of Wislicenus and Hentzschel.[6] This reaction was hastened by siphoning off the water layer occasionally as the concentration of sodium hydroxide increased, and adding fresh water. The yields never exceeded 30% and often ran lower. No cyclopentanone was recovered, the loss apparently being due chiefly to pinacone formation. Although several reduction units were maintained in simultaneous operation, the method was still very slow and required constant attention. It was therefore abandoned in favor of the catalytic method.

(2) With hydrogen and platinum-oxide platinum black catalyst, by the method of Adams and his co-workers. The procedure was essentially that described briefly by Adams and Noller[5] and more fully by Adams and Yohe,[12] using the apparatus described by Adkins and McElvain,[13] except that a 20-liter tank was used as the low-pressure hydrogen reservoir, and a quart ginger-ale bottle as reaction vessel, the latter being mounted in a cradle so designed as to reinforce it on all sides. From one to one and a half moles could be converted in this at a single run. The platinum oxide was prepared by the method of Adams and Voorhees.[14] From 1.5 to 2.5 g. of platinum oxide was placed in the reduction vessel, and 250 cc. of ethyl alcohol (95%) was added. Hydrogen at 3–4 atmospheres was applied, with shaking, for ten minutes, to reduce the oxide. Eighty-four grams (one mole) of freshly distilled cyclopentanone was then

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[11] "Organic Syntheses," John Wiley Sons, Inc., New York, Vol. V, **1925**, p. 9.

[12] Adams and Yohe, This Journal, **50**, 1503 (1928).

[13] Adkins and McElvain, "Practice of Organic Chemistry," McGraw-Hill Book Co., Inc., New York, **1925**, p. 277.

[14] Adams and Voorhees, This Journal, **44**, 1402 (1922). See also Adams and Shriner, *ibid.*, **45**, 2171 (1923).

added, hydrogen re-applied, and shaking continued until the drop in pressure indicated the required amount of absorption. The catalyst was then filtered off and the solution fractionated through an 86-cm. (34-inch) column; yield, 85–90%.[15]

Preparation of Cyclic Chlorides and Bromides.—Cyclopentyl and cyclohexyl chlorides were made by refluxing the corresponding alcohols with excess of concentrated hydrochloric acid. The former required three hours and the latter eighteen hours of refluxing for best results. A considerable quantity of cyclopentene was formed during the preparation of cyclopentyl chloride. The chlorides were washed with dilute sodium carbonate, dried and fractionated. Cyclopentyl bromide was prepared from cyclopentanol and phosphorus tribromide by the method of Adams and Noller.[5]

Preparation of Phosphorus Tribromide.—The method used was suggested but not described by Turner and Bury.[16] In a one-liter balloon flask fitted with a reflux condenser and a dropping funnel were placed 150 g. of carbon tetrachloride and 48 g. of finely divided red phosphorus. With cooling and frequent shaking, 360 g. of bromine was added drop by drop, after which the mixture was refluxed gently for fifteen minutes. It was then filtered and the filtrate distilled. The portion boiling between 170 and 175° was redistilled just before using, and the 173–175° fraction was employed in making cyclopentyl bromide. The yield, about 50%, was considerably less than that obtained in the usual way, by employing benzene and white phosphorus but it was obtained and purified with greater ease.

Preparation of Methyl Cyclopentyl Carbinol.—In a one-liter balloon flask, fitted with a dropping funnel, 70-cm. condenser, and motor-driven mercury-sealed stirrer, were placed 150 cc. of dry ether and 18 g. of magnesium turnings, and 77 g. (0.73 mole) of cyclopentyl chloride, in 120 cc. of ether, was added drop by drop. The reaction required cooling for a few minutes, and then continued to generate sufficient heat to maintain ebullition for nearly an hour. The solution was refluxed on a water-bath for an hour, allowed to stand for two hours surrounded with an ice-water-bath, and treated slowly with 33 g. of acetaldehyde in 120 cc. of ether. The mixture was allowed to stand overnight, refluxed for fifteen minutes and treated with crushed ice, followed by a slight excess of dilute hydrochloric acid. The ethereal portion was separated and combined with several ethereal extracts of the water layer. It was then washed with potassium carbonate solution, the wash liquid being subsequently extracted with ether, which was added to the main portion. After drying over two successive portions of potassium carbonate, the ether was distilled on a water-bath. The residue was placed in a flask

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[15] Information supplied by G. R. Yohe (private communication) and since published[11] was very helpful in carrying out this reduction. We noticed a number of peculiarities in the process, some of which merely corroborate Adams and Yohe's observations, and others which appear to be new. Reduction was decidedly more rapid in ethanol than in methanol. Addition of the ketone before reduction of the catalyst or repeated use of the same catalyst without re-solution and reprecipitation, caused a very marked diminution in yield, apparently greater than that experienced by Adams and Yohe. After a pronouncedly unsuccessful run, the use of anything involved in that run, catalyst, ketone, solvent or vessel, without rigorous purification, would usually spoil subsequent attempts. These observations seem to indicate that the catalyst was constantly undergoing slow poisoning from some undetermined source.

It was also noted that there was a rather sharp dividing line between the speed of shaking which gave maximum rate of conversion, and a speed which gave a much inferior rate. For best results, it was necessary for shaking to be sufficiently violent to throw the platinum particles to the surface of the solution, and to the walls of the vessel above the surface.

[16] Turner and Bury, *J. Chem. Soc.*, **123,** 2489 (1923).

with a 38-cm. (15-inch) fractionating column, and subjected to fractionation at reduced pressure. The principal cut was redistilled twice, ultimately yielding 11 g. of a colorless liquid, boiling at 85–85.5° at 52.5 mm. It had a pleasant penetrating odor, resembling that of menthol. Its constants are listed in the accompanying table. While the quantity obtained corresponds to a yield of only 13%, it is probable, taking into account losses through evaporation and comparing the quantities obtained in each successive fractionation, that the total amount of the carbinol formed in the reaction was about 40%.

Preparation of Ethyl, *n*-Propyl, *n*-Butyl and *n*-Hexyl Cyclopentyl Carbinols.—These were prepared as was the methyl compound, 1 mole of cyclopentyl bromide being used in each case except for the propyl, where it was only 0.3 mole. The addition of the amyl and heptyl aldehydes to the Grignard reagent gave comparatively little heat and the resulting complexes were soluble in ether. The yields were 19.5, 12, 18 and 11%, respectively, of the twice distilled products. The odors resembled that of the methyl compound except that the propyl suggested olives and the hexyl resembled *n*-heptanol.

Preparation of Phenyl Cyclopentyl Carbinol.—The reaction proceeded in the usual manner, except for the appearance of the crystals previously described, which were removed before distillation. A dark tarry residue remained when the ether was distilled and the higher-boiling liquid decanted. The latter was distilled from a Claisen flask at 5 mm. A fraction boiling between 129 and 131°, chiefly at 130°, was obtained, its distillation being accompanied by the appearance of a certain amount of decomposition. Freshly distilled, it possessed a light brown color, which changed, during a period of several weeks, to a very dark brown. A large quantity of tarry residue remained in the flask, and a little unchanged benzaldehyde was recovered. The yield of rather impure carbinol was about 7%.

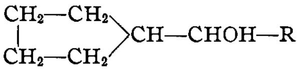
Attempt to Prepare Anisyl Cyclopentyl Carbinol.—The usual addition of the aldehyde produced only a small amount of heat. After removal of the condensation product previously described, the ether was distilled and the remaining liquid decanted and fractionated from a Claisen flask at 5–6 mm., to the accompaniment of much apparent decomposition. A rapidly-darkening, fairly constant-boiling cut of 12 g. was obtained in the neighborhood of 156° at 5–6 mm. On redistillation, decomposition was even more marked and the boiling point was not more definite. Analysis of the final product showed: C, 68.82; H, 8.07 (theoretical for anisyl cyclopentyl carbinol, C, 75.68; H, 8.80).

Preparation of Crystalline Derivatives of the Carbinols.—Attempts were made to prepare the 3,5-dinitrobenzoate, phenylurethan, and α-naphthylurethan of each carbinol. For the benzoate, half a gram of freshly prepared 3,5-dinitrobenzoyl chloride and a sufficient excess of the carbinol were dissolved in pyridine and heated at 100° for six hours. The solution was then filtered and the filtrate diluted with water until the ester precipitated. It was redissolved in warm 95% ethanol, boiled with finely ground charcoal, allowed to stand for an hour and filtered. Dilution and cooling precipitated the ester from the filtrate. Successive crystallizations were made from warm dilute alcohol.

The urethans were made by adding a sufficient excess of the carbinol to half a gram of the appropriate isocyanate, and heating the mixture in an oil-bath at 150° for six hours or more. The resultant urethan was dissolved in petroleum ether, filtered, reprecipitated by evaporation and taken up in warm methanol. Further crystallizations were made in the usual manner from either methanol or ethanol.

Summary

Alcohols of a new series, of the type



$$\begin{matrix} CH_2-CH_2 \\ | \\ CH_2-CH_2 \end{matrix}\!\!>CH-CHOH-R$$

have been prepared and characterized.

A side reaction indicating apparent steric hindrance in the formation of certain cyclic compounds has been studied.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

THERMAL DATA ON ORGANIC COMPOUNDS. VIII. THE HEAT CAPACITIES, ENTROPIES AND FREE ENERGIES OF THE ISOMERIC HEPTANES[1]

BY HUGH M. HUFFMAN,[2] GEORGE S. PARKS[3] AND S. BENSON THOMAS[4]

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Recently the nine isomeric heptanes have been prepared in a very pure form by Edgar, Calingaert and Marker.[5] Various physical properties of these samples were subsequently studied by a number of investigators, and much of the resulting data has been discussed and summarized by Edgar and Calingaert.[6] Through the courtesy of Dr. Edgar we have enjoyed the privilege of measuring the heat capacities of these isomers from liquid air temperatures up to that of the room. From the data thus obtained, the corresponding entropies and free energies have been calculated by means of the third law of thermodynamics. The present paper gives the results of our investigation.

In an earlier study dealing with a few isomeric organic compounds, two of us[7] suggested that "in the case of isomers the compound with the lowest melting point has the largest entropy and free energy." The present investigation, as well as the data recently obtained for three isomeric octanes,[8] does not support this suggestion. Rather it appears that in a group of isomers the entropy decreases systematically as the amount of branching increases. Thus the normal compound has always been found to have the largest entropy value. However, in the case of two isomers involving equal amounts of branching, it is usually true that the compound with the lower melting point has the larger entropy. At present no rule

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[1] This paper contains results obtained in an investigation of the heat capacities and free energies of some typical hydrocarbon compounds, listed as Project No. 29 of the American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by The Universal Oil Products Company. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

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[5] Edgar, Calingaert and Marker, THIS JOURNAL, **51**, 1483 (1929).

[6] Edgar and Calingaert, *ibid.*, **51**, 1540 (1929).

[7] Parks and Huffman, *ibid.*, **48**, 2788 (1926).

[8] Parks, Huffman and Thomas, *ibid.*, **52**, 1032 (1930).