Anal. Calcd. for $C_7H_{12}O_5$: C, 47.72; H, 6.87. Found: C, 48.04; H, 6.87.

The cinchonidine salt, m.p. 181.8–182.7°, was crystallized from ethyl acetate–methanol.

Anal. Calcd. for $C_{45}H_{56}O_7N_4$: C, 70.65; H, 7.37; N, 7.32. Found: C, 70.25; H, 7.81; N, 6.82.

The *p*-phenylphenacyl ester crystallized from ethanol–ethyl acetate, m.p. 131–132°.

Anal. Calcd. for $C_{35}H_{32}O_7$: C, 74.45; H, 5.71. Found: C, 73.86; H, 5.65.

The benzyl isothiuronium salt crystallized from acetone, m.p. 151.6–152.6.

Anal. Calcd. for $C_{21}H_{28}O_5N_4S_2$: C, 52.46; H, 5.87. Found: C, 52.37; H, 6.31.

Acknowledgment.—We wish to thank Mr. William A. Klemperer for determining the infrared spectra, and the Graduate Fellowship committee of the University of California for the award of the Abraham Rosenberg Fellowship to D. B. D.

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Dehydroxymethylation of Primary Alcohols

BY HERMAN PINES, H. G. RODENBERG[1] AND V. N. IPATIEFF[2]

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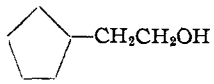
The dehydroxymethylation of 2-cyclopentylethanol, 1-methyl-1-hydroxymethylcyclohexane and 4-hydroxymethylcyclohexanol was studied at about 190° in the presence of a nickel–Kieselguhr catalyst and under 100 atmospheres of hydrogen pressure. The respective products in 80–100% yield obtained from this reaction were methylcyclopentane, methylcyclohexane and cyclohexanol.

It was shown previously[3] that the dehydroxymethylation of primary alcohols proceeds in the presence of a nickel catalyst and hydrogen according to the general formula

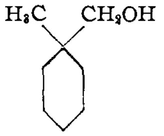
$$RCH_2OH + H_2 \longrightarrow RH + CH_4 + H_2O$$

Thus good yields of neopentane were obtained from 3,3-dimethylbutanol,[3a] 6,6-dimethylnorpinane from myrtanol,[3b] pinane from nopol[3b] and cyclobutane from cyclobutylmethanol.[3c]

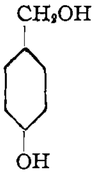
In order to determine the applicability of this reaction, as a method of degradation of primary alcohols, this study was extended to three other representative types of alcohols, namely, to: (1) 2-cyclopentylethanol (I), which on hydrogenolysis in the presence of nickel–alumina catalyst undergoes a skeletal rearrangement forming methylcyclohexane[3a]; (2) 1-methyl-1-hydroxymethylcyclohexane (II), in which the hydroxymethyl group is attached to a tertiary carbon atom; and (3) 4-hydroxymethylcyclohexanol (III), which besides a hydroxymethyl group contains also a secondary hydroxy group.



I



II



III

The experiments were carried out according to the procedure described previously[3] using nickel–Kieselguhr catalyst and initial hydrogen pressure of 100 atmospheres.

Compound I underwent 93% reaction at 171–190° forming, according to infrared spectral analysis, methylcyclopentane as the only liquid hydrocarbon. Compound II underwent over 90% hydrogenolysis at 194° forming methylcyclohexane. The hydrogenolysis of compound III proceeds stepwise; the dehydroxymethylation occurs at a lower temperature than the hydrogenolysis of the hydroxy group attached to the ring. At 174°, 80% of compound III reacted to form only cyclohexanol. At 208° the reaction went to completion and the product consisted of 55% cyclohexane and 40% cyclohexanol.

The present results and those obtained from previous study show that the dehydroxymethylation method could be used as an indirect method for degradation of acids, if the latter are reduced to the corresponding alcohols.

Experimental Part

Dehydroxymethylation.—The dehydroxymethylation reactions were made in a 450-ml. capacity rotating autoclave. The carbinol, 0.1–0.3 mole, and 10% by weight of UOP nickel–Kieselguhr catalyst[4] were placed in the autoclave and heated in the presence of 100 atmospheres of initial hydrogen pressure. The experimental results are summarized in Table I. The gases recovered from the reaction consisted, according to mass spectrographic analyses, of hydrogen and methane.[5] Only about 0.1–0.2% of carbon monoxide was formed.

The structures of the compounds produced were determined by physical constants and infrared spectral analyses.

TABLE I

DEHYDROXYMETHYLATION OF PRIMARY ALCOHOLS

Expt.	Alcohol used	Conditions of reacn. Temp., °C.	Hr.	Alcohol reacted, %	Product formed
1	I	171	19	100	Methylcyclopentane
2	I	190	5	94	Methylcyclopentane
3	II	194	3	94	Methylcyclohexane
4	III	174	6	80	Cyclohexanol
5	III	208	9	100	55% Cyclohexane 40% Cyclohexanol

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[1] Universal Oil Products Company Research Fellow, 1951.

[2] Deceased, November 29, 1952.

[3] (a) V. N. Ipatieff, W. W. Thompson and H. Pines, THIS JOURNAL, **73**, 553 (1951); (b) V. N. Ipatieff, G. Czajkowski and H. Pines, *ibid.*, **73**, 4098 (1951); (c) H. Pines, H. G. Rodenberg and V. N. Ipatieff, *ibid.*, **75**, 6065 (1953).

[4] V. N. Ipatieff and B. B. Corson, *Ind. Eng. Chem.*, **26**, 1838 (1934).

[5] The mass spectrographic analyses were made by J. B. Grutka, Universal Oil Products Company.

Preparation of Material

2-Cyclopentylethanol (I). 1.—Ethyl cyclopentylideneacetate was prepared in 17% yield by the Reformatsky reaction from two moles of cyclopentanone, according to the usual procedure.[6] The product distilled at 81–91° at 10 mm.

2.—Ethyl cyclopentylacetate was prepared in 91% yield by hydrogenating ethyl cyclopentylideneacetate at 120° under 100 atmospheres of pressure in the presence of 10% by weight of copper chromite catalyst.[7] It distilled at 77–79° at 11 min., $n^{20}\text{D}$ 1.4430.

3.—2-Cyclopentylethanol was obtained in 93% yield by reducing the acetate with lithium aluminum hydride. The carbinol distilled at 178°, $n^{20}\text{D}$ 1.4642 (b.p. 179–181°, $n^{20}\text{D}$ 1.4615[3a]).

1-Methylcyclohexylmethanol (II).—Compound II was prepared in 87% yield by hydrogenating 4-methyl-4-formylcyclohexene[8] under 100 atmospheres of hydrogen pressure at 90° and in the presence of nickel–Kieselguhr catalyst. The alcohol distilled at 186–189°, $n^{20}\text{D}$ 1.4672.

Anal. Calcd. for $C_8H_{16}O$: C, 75.00; H, 12.50. Found: C, 74.26; H, 12.24.

The **3,5-dinitrobenzoate** of the alcohol melted after crystallization from ethanol at 76–77°.

Anal. Calcd. for $C_{15}H_{18}O_6N_2$: N, 8.69. Found: N, 8.63.

4-Hydroxycyclohexanemethanol (III). 1. **4-Carbethoxycyclohexanol** was obtained in 72% yield by hydrogenating 0.6 mole of ethyl *p*-hydroxybenzoate dissolved in 300 ml. of ethanol. The hydrogenation was carried out at 170° under 100 atmospheres of initial hydrogen pressure and in the presence of nickel–Kieselguhr catalyst. The product distilled at 142–145° (14 min.), $n^{20}\text{D}$ 1.4666.

2. **4-Hydroxycyclohexylmethanol** was prepared by reduction of the ester with lithium aluminum hydride. From 75 g. of the ester, 15 g. of the solid *trans* isomer of III was obtained, which on crystallization from an acetone–ether solution melted at 102°, as compared to 103° reported previously.[9] The mother liquor, 28 g., consisted of a mixture of *cis* and *trans* isomer, which distilled at 133–135° at 3 min., $n^{20}\text{D}$ 1.49920. The total yield of the alcohol was 77%. The mixture of the isomers was used for dehydroxymethylation reaction.

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[6] R. L. Shriner, "Organic Reactions," edited by R. Adams, Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, pp. 1–37.

[7] H. Adkins and E. E. Burgoyne, THIS JOURNAL, **71**, 3528 (1949), ref. 2.

[8] H. Pines, F. J. Pavlik and V. N. Ipatieff, *ibid.*, **73**, 5738 (1951).

[9] L. N. Owen and P. A. Robins, *J. Chem. Soc.*, 326 (1949).

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN]

Ionic Polymerization.[1] Ion Pair Chain Mechanisms. The Effect of Different Lewis Acid Catalysts on the Monomer Reactivity Ratios in Copolymerization

BY C. G. OVERBERGER, R. J. EHRIG[2] AND DAVID TANNER

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With the copolymer system styrene–*p*-chlorostyrene in solvent mixtures of carbon tetrachloride and nitrobenzene, no difference in monomer reactivity ratios were obtained with aluminum bromide, ferric chloride, titanium tetrachloride, stannic chloride and titanium tetrachloride–trichloroacetic acid as catalysts in homogeneous solution. In these solvent systems with the above catalysts no measurable fragments from the solvent or catalysts were incorporated in purified polystyrenes obtained from styrene alone with the exception of aluminum bromide in pure nitrobenzene as a solvent and antimony pentachloride in a 1:1 carbon tetrachloride–nitrobenzene solution. The insensitivity of monomer reactivity ratios in this system to changes in dielectric constant and catalyst concentration previously noted with a stannic chloride catalyst was verified with other catalysts.

In a previous paper, the effect of reaction conditions on the monomer reactivity ratios for the copolymerization of styrene and *p*-chlorostyrene was investigated in order to use this technique to study the mechanism of ion pair addition to the double bond.[3] An important variable which was not included in the previous work is the effect of variation in types of catalyst. Information of this type was sought in order to aid in the elucidation of the mechanism of the propagation step.[1] In addition, it was desirable to determine whether any fragments from the catalysts or solvent remained in the polymer chain after purification. This paper reports the monomer reactivity ratios obtained for the system styrene–*p*-chlorostyrene in carbon tetrachloride–nitrobenzene mixtures or in pure nitrobenzene for ferric chloride, titanium tetrachloride, titanium tetrachloride–trichloroacetic acid and aluminum bromide. Additional data obtained with stannic chloride in pure nitrobenzene and with aluminum bromide in pure carbon tetrachloride also are reported. The anomalous behavior of antimony pentachloride is noted.

Experimental

Solvents and Monomers.—Carbon tetrachloride, nitrobenzene, styrene and *p*-chlorostyrene were purified as described previously.[3]

Catalysts.—Stannic chloride was purified and ampules prepared according to the procedure described previously.[3]

Titanium tetrachloride, C.P. (Eimer and Amend), was purified in the same manner as the stannic chloride except that the titanium tetrachloride was refluxed with a small amount of very fine, pure copper strips to remove the last traces of light color[4] in the titanium tetrachloride. The titanium tetrachloride was distilled under nitrogen and ampules were prepared in a nitrogen atmosphere as previously described.[3] The filled ampules were colorless.

Anhydrous ferric chloride, C.P. (Eimer and Amend), was purified by sublimation in an apparatus similar to that described for the preparation of the Lewis acid by Tarr.[5] A few minor changes were necessary. After the apparatus was flame dried, ferric chloride was quickly put into the reaction chamber. This entire apparatus was then swept with dry nitrogen and again flame dried. If any yellow

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[1] This is the third in a series of papers concerned with ionic polymerization. For the second paper, see C. G. Overberger, L. H. Arond, D. Tanner, J. J. Taylor and T. Alfrey, Jr., THIS JOURNAL, **74**, 4848 (1952). A portion of this work was supported by a contract from the Office of Naval Research.

[2] A portion of a thesis submitted by R. J. Ehrig in partial fulfillment of the requirements for the degree of Master of Science to the graduate school of the Polytechnic Institute of Brooklyn.

[3] C. G. Overberger, L. H. Arond and J. J. Taylor, THIS JOURNAL, **73**, 5541 (1951).

[4] C. K. Stoddard and E. Pietz, U. S. Bur. Mines, Rept. Invest. 4153, 1947; see *C. A.*, **42**, 2406 (1948).

[5] B. R. Tarr, "Inorganic Syntheses," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 191.