XXXII (34 g., 0.10 mole) was added over 43 hours to 9.2 g. (0.40 mole) of sodium stirred at 6500 r.p.m. to give 21.35 g. of polymer and an oil. The oil was dissolved in benzene and extracted with 5% sodium carbonate solution. Acidification of the extracts with concentrated hydrochloric acid gave 1.3 g. of 1,3-bis-(4-carboxymethylphenyl)-propane. The benzene was removed from the organic layer and the oil was caused to solidify at −80° and recrystallized from petroleum ether (b.p. 60–70°) to give 5.2 g. of the starting ester. The filtrate from the recrystallization was taken to dryness and the residual oil was distilled to give 0.94 g. of XVI (b.p. 170–215° at 0.3 mm.) and 0.76 g. of the starting ester (b.p. 240–270° at 0.3 mm.)

Addition of 19 g. (0.056 mole) of XXXII to 5 g. (0.217 mole) of sodium over three hours using toluene as the solvent gave 1 g. of polymer and 0.5 g. of 1,3-bis-(4-carboxymethylphenyl)-propane. Solidification of the usual residual oil and chromatography of the solid on alumina in benzene solution gave eluates, the early fractions of which yielded 0.1 g. of white plates (acetone), m.p. 117–118° (XXXVII).

Recrystallization from acetone of the residues from the later fractions gave 0.09 g. of white needles melting at 142–143° (XL).

Acknowledgment.—The authors are happy to acknowledge the value of conversations concerning the substance of this paper with Drs. K. N. Trueblood, W. G. McMillan and R. L. Scott. The analyses reported were done by Mrs. Bea Kent and Dr. A. Elek.

LOS ANGELES 24, CALIF. RECEIVED MARCH 19, 1951

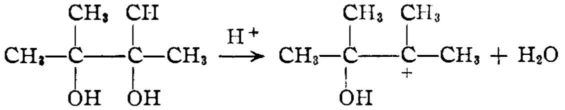
[CONTRIBUTION FROM THE SYNTHETIC FUELS RESEARCH BRANCH, BUREAU OF MINES]

Chemistry of the Oxo and Related Reactions, V, Acid Catalysis with Pinacol

BY IRVING WENDER, SOL METLIN AND MILTON ORCHIN

The reaction of pinacol with carbon monoxide and hydrogen at 185° in the presence of a cobalt catalyst gives a complex mixture of products. Four compounds more volatile than the starting material were identified; these were pinacolone, pinacolyl alcohol, 3,4-dimethylpentanol-1 and 2,2,3-trimethyltetrahydrofuran. The origin of these compounds is consistent with the formation and further reaction of a common carbonium-ion intermediate formed from pinacol under acidic conditions. The acid catalyst is probably cobalt hydrocarbonyl, $HCo(CO)_4$.

To substantiate the postulate that the homologation of alcohols with excess synthesis gas at 185° in the presence of cobalt is catalyzed by the acid $HCo(CO)_4$,[1] the reaction of pinacol with synthesis gas was examined. The pinacol–pinacolone rearrangement is a known example of an acid-catalyzed reaction. If the homologation reaction is similarly catalyzed, the transient carbonium ion (A) should be formed from pinacol



$$CH_3-\underset{OH}{\overset{CH_3}{C}}-\underset{OH}{\overset{CH}{C}}-CH_3 \xrightarrow{H^+} CH_3-\underset{OH}{\overset{CH_3}{C}}-\underset{+}{\overset{CH_3}{C}}-CH_3 + H_2O$$

A

A study of the products of the reaction of pinacol with synthesis gas resulted in the isolation and identification of the following compounds: pinacolone (I), pinacolyl alcohol (II), 3,4-dimethylpentanol-1 (III) and 2,2,3-trimethyltetrahydrofuran (IV). All of these products may be derived from the postulated intermediate (A) according to the scheme outlined in Chart I.

Experimental

The Reaction of Pinacol with Carbon Monoxide and Hydrogen.—A solution of 74 g. (0.63 mole) of pinacol (b. p. 85.0–85.5° at 21 mm.) and 10 g. of dicobalt octacarbonyl in 80 ml. of benzene was placed in a 500-ml. stainless-steel autoclave. Synthesis gas ($2H_2$:1CO) was added until the pressure reached 3200 p. s. i. (3.3 moles of gas). The autoclave was heated, with rocking, to 185° within 160 minutes; the maximum pressure obtained was 4350 p. s. i. at 164°. The temperature of the autoclave was held at 185–189° for 4 hours, during which time the pressure dropped to 2600 p. s. i. The reaction vessel was cooled to 25°; the pressure at this temperature was 1500 p. s. i. This pressure drop corresponded to approximately 1.7 moles of gas, or 2.7 moles of gas per mole of pinacol. The gases were then discharged.

The reaction products were washed from the autoclave with benzene, and 11.5 ml. of an aqueous layer was removed from the products. The benzene solution was then distilled in a one-foot, glass, concentric tube column. Another 3.9 ml. of water distilled over as the benzene–water azeotrope; the total amount of water recovered was 15.4 ml. (0.86 mole).

Distillation of the remaining products yielded a fraction, b.p. 82–106°, which contained approximately 10.8 g. (17.2%) of pinacolone (by hydroxylamine hydrochloride titration) and 1.1 g. of pinacolyl alcohol. Addition of 2,4-dinitrophenylhydrazine to this fraction yielded the 2,4-dinitrophenylhydrazone of pinacolone, m. p. 126.2–127.6°, not depressed when mixed with an authentic sample. A 3.1-g. fraction boiling from 106–129° was mainly pinacolyl alcohol, but a small amount of another substance, probably 2,2,3-trimethyltetrahydrofuran, was present. Addition of phenyl isocyanate to this solution yielded the phenylurethan of pinacolyl alcohol, m. p. 74.8–76.7°, not depressed when mixed with the phenylurethan of pinacolyl alcohol prepared by lithium aluminum hydride reduction of pinacolone. A total of 4.2 g. (4.1%) of pinacolyl alcohol was obtained.

Distillation of the residue at atmospheric pressure in the same column yielded 19.1 g. (26.2%) of impure 3,4-dimethylpentanol-1, b. p. 164.5–166.0°, $n^{25}D$ 1.4290. The melting point of the dinitrobenzoate prepared from this fraction was 50.2–51.9°[2]; the dinitrobenzoate formed an addition compound with α-naphthylamine, which softened at 73.5° and melted at 76–77°.[2] A residue of 22.9 g. remained.

Attempted Thermal Rearrangement of Pinacol.—Seventy-four grams (0.63 mole) of pinacol, 80 ml. of benzene and 3 g. of $CoCO_3$ were placed in the autoclave. The bomb was filled with 3200 p. s. i. of nitrogen and heated at 185° for 4 hours. The products of the reaction were filtered and distilled in the 1-foot, glass, semi-micro column. After the benzene was removed, the boiling point rose sharply to 174°, and the first distillate at this temperature solidified in the receiver. 63.9 g. (86.4%) of the starting material was recovered unchanged. There was no other product.

Tetrahydrofurfuryl Alcohol from 1,2,5-Trihydroxypentane.—Eighteen grams (0.15 mole) of 1,2,5-trihydroxypentane,[3] 21 ml. of benzene, 100 ml. of ether and 2.7 g. of $[Co(CO)_4]_2$ were treated at 180–185° for 3 hours in an autoclave with 3,000 p. s. i. of 1:1 synthesis gas. Distillation of the reaction products from a Claisen flask yielded 3.9 g.

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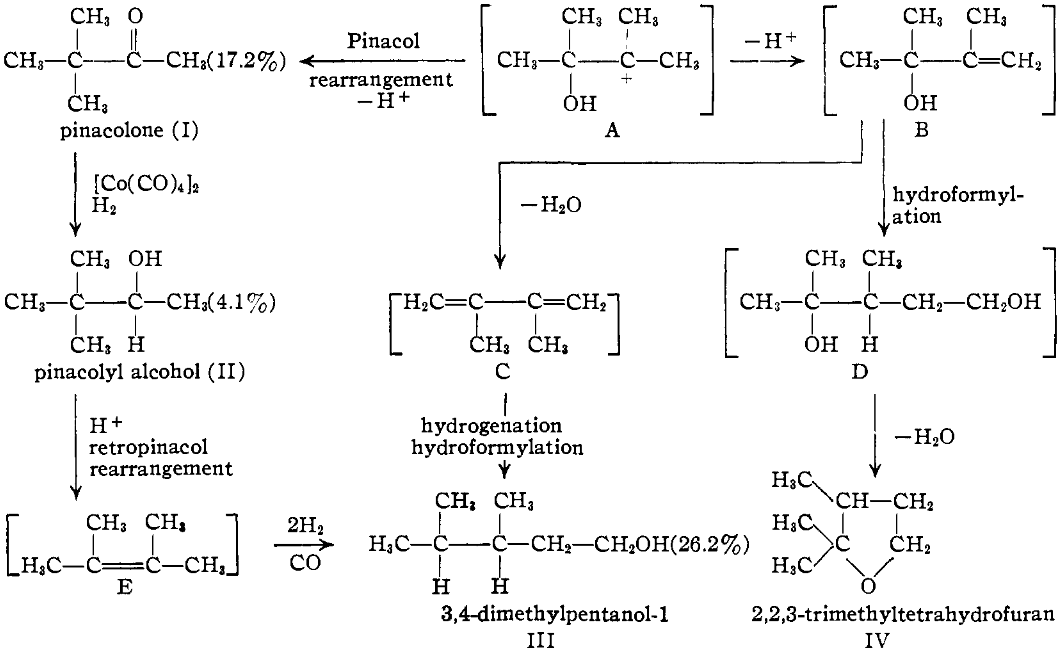
[1] I. Wender, R. Levine and M. Orchin, THIS JOURNAL, 71, 4160 (1949).

[2] L. Schmerling, *ibid.*, 67, 1440 (1945).

[3] O. Grummitt, J. A. Stearns and A. A. Arters, "Organic Syntheses," Vol. 29, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 89.

CHART I



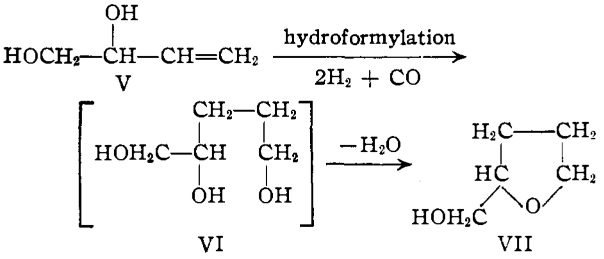
(25.5%) of tetrahydrofurfuryl alcohol; the phenylurethan, m.p. 56.1–57.0°, was not depressed by an authentic sample.

Discussion

The four products identified in the reaction of pinacol may be accounted for by a series of reactions involving acid catalysis. It has been shown that cobalt hydrocarbonyl, $HCo(CO)_4$, is a strong acid.[4] The suggested mode of formation of pinacolone is apparent from Chart I. Previous work has shown that aliphatic ketones are reduced slowly to alcohols in the presence of dicobalt octacarbonyl and synthesis gas[5]; a similar reduction of pinacolone accounts for the formation of pinacolyl alcohol.

3,4-Dimethylpentanol-1 (III).—Loss of a proton from A prior to rearrangement could give the unsaturated alcohol (B). This alcohol was not isolated, but it is likely that dehydration to 2,3-dimethylbutadiene would occur[6] under the acidic conditions of the reaction. It has been established that the hydroformylation of 2,3-dimethylbutadiene yields 3,4-dimethylpentanol-1.[7,5] As the conditions of the present reaction were nearly identical with those for hydroformylation, the postulated series of reactions (Chart I) accounts for the formation of 3,4-dimethylpentanol-1 (III). An alternate but less likely route to III consists of the retropinacolic rearrangement of pinacolyl alcohol (II) followed by hydroformylation of the resulting tetramethylethylene.[8]

2,2,3-Trimethyltetrahydrofuran (IV).—The formation of a tetrahydrofuran system from an acyclic compound has been reported; 3-butene-1,2-diol (V), an unsaturated alcohol structurally similar to B, gave tetrahydrofurfuryl alcohol (VII), according to the postulated series of reactions[9]



Corroboration for the transformation of VI to VII was obtained in the present investigation. 1,2,5-Trihydroxypentane (VI) was synthesized and treated with synthesis gas and dicobalt octacarbonyl at 185°; tetrahydrofurfuryl alcohol (25.5%) was, indeed, obtained. If B is an intermediate in the reaction of pinacol with synthesis gas, a similar reaction should yield the diol D, which, by a mechanism analogous to the conversion of VI to VII, could lose water to yield 2,2,3-trimethyltetrahydrofuran (IV). Examination in the mass spectrometer[10] of the fraction boiling from 106–129° showed (a) no mass peaks above 102, (b) peaks at 102 (pinacolyl alcohol) and 100 (pinacolone) and (c) a large peak at 99. The 99 peak was not present in the spectra of pure pinacolyl alcohol or pinacolone. This peak probably resulted from an ionization process, as no compound containing carbon (atomic mass 12), hydrogen (atomic mass 1) and oxygen (atomic mass 16) can have an odd number as its molecular weight. The loss of CH_3 (mass 15) from 2,2,3-trimethyltetrahydrofuran (IV), molecular weight

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(4) J. W. Copenhaver and M. H. Bigelow, "Acetylene and Carbon Monoxide Chemistry," Reinhold Publishing Corp., New York, N. Y., 1949, p. 288.

(5) I. Wender, R. Levine and M. Orchin, THIS JOURNAL, 72, 4375, (1950).

(6) C. F. H. Allen and Alan Bell, "Organic Syntheses," Vol. 22, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 39.

(7) H. Adkins, Abstracts of the Eleventh National Organic Chemistry Symposium of the American Chemical Society, University of Wisconsin, June, 1949.

(8) A. I. Keulemans, A. Kwantes and T. H. Van Bavel, *Rec. trav. chim.*, 67, 298 (1949).

(9) L. E. Craig, R. M. Elofson and I. J. Ressa, THIS JOURNAL, 72, 3277 (1950).

(10) We wish to thank Dr. R. A. Friedel and Mr. A. G. Sharkey for the determination and interpretation of the mass spectra data.

114, would give a 99 peak. The failure to obtain a peak at 114 corresponding to a molecular weight of IV is not unexpected, as many compounds fail to give peaks corresponding to their molecular weight.

To eliminate the possibility that a thermal rearrangement of pinacol to pinacolone occurred at 185°, pinacol was heated at this temperature with 3200 p.s.i. of nitrogen in the presence of a cobalt catalyst. No rearrangement occurred, and 85% of the starting material was recovered unchanged.

The evidence strongly indicates that acid-catalyzed reactions can occur in the system comprising synthesis gas and a cobalt catalyst at about 185°. This acid is very likely cobalt hydrocarbonyl, which is in equilibrium with dicobalt octacarbonyl

$$[Co(CO)_4]_2 + H_2 \rightleftarrows 2HCo(CO)_4$$

BRUCETON, PENNA. RECEIVED MARCH 30, 1951

[CONTRIBUTION FROM THE WESTERN REGIONAL RESEARCH LABORATORY][1]

Enzymatic Browning of Fruits. II. Dissociation Constants of Substituted Catechols

BY JOSEPH CORSE AND LLOYD L. INGRAHAM

The dissociation constants of several substituted catechols have been measured in aqueous dioxane solution. In the correlation of the dissociation constants by Hammett's $\rho\sigma$ treatment, better agreement was found using average values of σm and σp than by using the most acid strengthening σ.

In connection with work on the oxidation of catechols, it has been necessary to know the relative dissociation constants of certain substituted catechols. Because of the low solubility of some of the compounds in water, the dissociation constants were determined by titration with 0.1 *N* base in 40% dioxane (prepared by adding 400 ml. of dioxane to 600 ml. of water). The *p*H changes during titration were measured by means of a glass electrode which was calibrated by aqueous buffers. The values thus found in aqueous dioxane are only relative and a correction of 0.04 *pK* unit has been added in order to obtain the true hydrogen ion activity in 40% dioxane. This factor was evaluated by the method of Dole[2] using the vapor pressure data of Hovorka, Schaefer and Dreisbach.[3]

The *pK* values were calculated from the *p*H obtained after addition of one-half mole of base per mole of acid from the equation

$$pK = p\text{H} - \log \frac{(\text{Na}^+) + (\text{H}^+) - (\text{OH}^-)}{(\text{Na}^+) - (\text{H}^+) + (\text{OH}^-)}$$

Each *pK* shown in Table I represents the value obtained from a discrete titration curve. *pK* values above 11.4 cannot be evaluated accurately and are only reported as greater than 11.4.

Experimental

Materials.—The catechols used in this study were purified commercial chemicals or were prepared by methods described in the literature and are noted in Table I.

Titrations.—Approximately 0.4 millimole of the catechol in 40 ml. of 40% dioxane[4] was titrated with 0.1 *N* aqueous carbonate-free sodium hydroxide, using a 5-ml. buret. The calculated amount of pure dioxane was added to the catechol solution at the beginning of the titration to obtain a 40% dioxane solution at the half-equivalence point. The *p*H was determined with a glass electrode and a Beckman model G *p*H meter. At *p*H values greater than 10.5 a "blue type E" Beckman glass electrode was used. The glass electrodes were standardized against 0.05 *N* potassium acid phthalate (*p*H assumed to be 4.00 at 25.0°). The titration vessel was jacketed with water at 25.0°, and nitrogen purified with Fieser's solution[5] was passed through the titration cell to prevent oxidation. The nitrogen rate of flow was such that if it were stopped no noticeable change was observed on the *p*H meter. With the type E glass electrode the flow had to be stopped entirely to obtain a reading.

Discussion

An attempt was made to relate the dissociation constants by Hammett's[6] $\rho\sigma$ treatment for those substituents whose σ values are known. However, since a substituent in a 4-substituted catechol is both meta and para to a phenolic hydroxyl group, it is not immediately apparent which value (σ_m or σ_p) should be used to calculate the dissociation. An initial assumption is to use the most acid strengthening (higher) σ value; this assumes that the corresponding hydrogen ionizes and that the other hydroxy group (ortho to the ionized group) remains a constant factor throughout the series. For catechol itself, we no longer know which hydrogen leaves, and the dissociation constant must be corrected by a statistical factor of 2.

The data treated in this manner are shown in Fig. 1. The least squares line through these points gives $pK_0 = 11.12$, $\rho = 2.703$ and a standard error[7] of 0.16 in *pK*.

A better fit is obtained if an average value of σ_m and σ_p is used. This treatment is shown in Fig. 2. The least squares line in this case gives $pK_0 = 10.84$, $\rho = 3.299$ and a standard error in *pK* of 0.07. This treatment probably owes its success to the fact that the intramolecular hydrogen bonding in the catechol causes strong interaction between the oxygens. A substituent affecting the charge on one oxygen must also affect the other oxygen. The loss of either proton must give the same ion.

It is fully realized that with a substituent the

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(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) Malcolm Dole, "The Glass Electrode," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 276.

(3) F. Hovorka, R. A. Schaefer and O. Dreisbach, THIS JOURNAL, **58**, 2264 (1936).

(4) Purified by the method described in L. F. Fieser, "Experiments in Organic Chemistry," 2nd Ed., D. C. Heath and Co., New York, N. Y., 1941, p. 368.

(5) Reference 4, p. 395.

(6) L. P. Hammett, "Physical Organic Chemistry," Chapter VII, McGraw-Hill Book Co., Inc., New York, N. Y., 1940.

(7) F. C. Mills, "Statistical Methods," Henry Holt and Company, New York, N. Y., 1940, p. 330.