

erization experiments with optically active adducts in an attempt to find a basis for favoring one description over the other.¹⁵

(15) Diene additions of anthracenes to maleic anhydride involve preliminary (or competing), rapidly reversible complex formation between the addends [L. J. Andrews and R. M. Keefer, *THIS JOURNAL*, **77**, 6284 (1955)]. It should be pointed out that a maleic anhydride-cyclopentadiene complex that was in such rapid equilibrium with the addends could not account for path A. Thus, in our case, either the

Acknowledgment.—We are indebted to the Office of Ordnance Research for financial support, and to Professors S. W. Benson and G. S. Hammond for helpful comments.

M-C complex is protected by a higher barrier for dissociation than are the complexes in the anthracene cases, or else the "cage effect" is the detailed description of path A.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF MARYLAND]

The Pinacol Rearrangement of *meso*- and *dl*-3,4-Dimethyl-3,4-hexanediol

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RECEIVED JUNE 25, 1956

The pinacol-pinacolone rearrangement of 3,4-dimethyl-3,4-hexanediol has been studied, and the pinacolone mixture found to consist of 70–73% of the ketone resulting from the migration of an ethyl group, regardless of whether one started with the solid *meso*-pinacol or the liquid *dl*-isomer. The *meso*-form of the pinacol gives a 50% yield of the mixture of ketones whereas the *dl*-rich, liquid mixture, containing some of the *meso*-form, gives only a 17% yield.

Four different investigators¹ have studied the pinacol-pinacolone rearrangement of 3,4-dimethyl-3,4-hexanediol. It was finally demonstrated by Nybergh^{1d} that, contrary to the conclusions reached by the three previous investigators, the rearrangement involved the preferential migration of an ethyl group rather than a methyl group.

As the first step in a systematic study of the rearrangement of non-cyclic aliphatic, symmetrical pinacols, we have reinvestigated the rearrangement of this compound and have determined the composition of the mixture of isomeric pinacolones by an analytical method different from that employed by Nybergh. We find that the mixture consists of about 70–73% of the methyl ketone regardless of whether the starting material is the pure solid form of the pinacol, assumed to be the *meso*-form, or the liquid mixture which is rich in the isomeric *dl*-form but contains a presumably small but unknown amount of the *meso*-form. Nybergh estimated the two pinacolones to be formed in the ratio of four of the methyl ketone to one of the ethyl ketone when starting with the solid *meso*-form; he did not examine the liquid form.

We were surprised to find that the yield of the mixture of pinacolones from the *meso*-form of the pinacol was 50% of the theoretical, whereas under the same conditions (pinacol dissolved in an excess of concentrated sulfuric acid at -10° for two hours) the yield of the mixture of pinacolones from the liquid pinacol mixture was only 17%. Inasmuch as an examination of molecular models indicates there should be free rotation between the two central carbon atoms, this result is most interesting. It is reminiscent of the differences Bartlett² observed in the rearrangement of *cis*- and *trans*-cyclic pinacols, but is not as pronounced. In the case of the rearrangement of the liquid pinacol mixture, much material is obtained distilling higher than the expected pinacolones. The *meso*-form also gives

a high boiling fraction, but in lesser amounts. These high boiling fractions were combined, purified by distillation, and the fraction distilling at 249–254 $^{\circ}$ at 760 mm. found to have a molecular weight and carbon-hydrogen analysis corresponding to a C₁₆H₂₈ unsaturated hydrocarbon. It gave the usual qualitative tests for unsaturation.

Our method of analyzing the mixture of pinacolones involved synthesizing reference compounds, *t*-amylethylcarbinol and 3-ethyl-3-methyl-2-pentanol, with which the carbinols obtained from the hydrogenation of the pinacolone mixtures could be compared. *t*-Amylethylcarbinol is the carbinol corresponding to one of the isomeric pinacolones; it was prepared by the Grignard reaction of *t*-amylmagnesium chloride on propionaldehyde. The other carbinol, 3-ethyl-3-methyl-2-pentanol, could not be obtained by a similar Grignard reaction, but was finally prepared by hydrogenating some pure 3-ethyl-3-methyl-2-pentanone. This had been obtained in a crude state from the pinacol rearrangement of 3,4-dimethyl-3,4-hexanediol, purified by repeated recrystallization of the semicarbazone derivative, and finally reconverted to the pure ketone by acid hydrolysis. The two isomeric alcohols were proven to be different by preparing their phthalic acid esters, m.p. 70 and 110 $^{\circ}$, respectively. The pinacolone mixtures obtained from the rearrangement were purified by steam distillation followed by fractional distillation, and then quantitatively hydrogenated to the mixture of alcohols. The composition of these mixtures was deduced by comparing their infrared absorption spectra with those of the pure isomers.

Experimental

All melting points are corrected. Analyses are by Mrs. Mary Aldridge and Miss Kathryn Gerdeman.

***t*-Amylethylcarbinol.**—*t*-Amylmagnesium chloride in an ether solution, standardized by titrating an aliquot with standard acid, was allowed to react with an equivalent amount of propionaldehyde in a nitrogen atmosphere under the usual Grignard conditions. From 4.5 moles, there was obtained 37 ml., b.p. 67 $^{\circ}$ at 19 mm., n_D^{20} 1.4320. The carbon analysis was 0.7% low. The material was purified through the phthalic acid ester prepared by heating 20 g. of the carbinol with 20 g. of phthalic anhydride at 110 $^{\circ}$ for 15

(1) (a) G. Lawrinowitsch, *Ann.*, **185**, 123 (1877); (b) P. Herschmann, *Monatsh.*, **14**, 233 (1893); (c) B. Braun and H. Kittel, *Monatsh.*, **27**, 803 (1906); (d) B. Nybergh, *Ber.*, **55B**, 1960 (1922).

(2) (a) P. D. Bartlett and A. Bavley, *THIS JOURNAL*, **60**, 2416 (1938); (b) P. D. Bartlett and R. F. Brown, *ibid.*, **62**, 2927 (1940).

hours, dissolving in 5% sodium carbonate solution, washing the solution with ether, removing the ether by aeration, acidifying and extracting the ester with chloroform. After recrystallizing from chloroform, there was obtained 15 g. (36% yield) of the phthalic acid ester, m.p. 68.5–71°.

Anal. Calcd. for $C_{16}H_{22}O_4$: C, 69.29; H, 7.68. Found: C, 69.11; H, 7.87.

On refluxing 15 g. of the ester with 15% sodium hydroxide solution for four hours, there was obtained a 50% yield of the *t*-amylethylcarbinol, b.p. 67° at 20 mm., n^{25}_D 1.4315.

Anal. Calcd. for $C_{20}H_{34}O$: C, 73.78; H, 13.93. Found: C, 73.57; H, 13.71.

3-Ethyl-3-methyl-2-pentanol.—The pinacol, 3,4-dimethyl-3,4-hexanediol (100 g.), was prepared and the mixture of isomers rearranged as described below. The mixture of ketones obtained (37 g.) was dissolved in 220 ml. of methanol and allowed to react with equivalent amounts of sodium acetate and semicarbazide hydrochloride in 70 ml. of water. After standing overnight at 0°, 34 g. of white crystals of the semicarbazone of 3-ethyl-3-methyl-2-pentanol was obtained, m.p. 173° after recrystallization from a 1:1 water-ethanol mixture; reported m.p., 168°. ¹⁴

Anal. Calcd. for $C_9H_{19}N_3O$: C, 58.34; H, 10.33; N, 22.69. Found: C, 58.56; H, 10.42; N, 22.61.

The ketone was regenerated from the semicarbazone by steam distilling a mixture of 24 g. of the semicarbazone and 100 ml. of 20% sulfuric acid. On distillation of the water-insoluble product, 15 g. was obtained (91% yield), b.p. 152–153°, n^{25}_D 1.4190; reported ¹⁴ b.p. 151.5°.

The alcohol was obtained by hydrogenating 14 g. of the ketone dissolved in 23 ml. of anhydrous ether over 0.7 g. of copper chromite catalyst at 150° for 3 hr. and at an initial pressure of 200 atm. of hydrogen. On distillation, 14 g. (98% yield) of the 3-ethyl-3-methyl-2-pentanol was obtained, b.p. 87° at 39 mm., n^{25}_D 1.4379.

Anal. Calcd. for $C_9H_{18}O$: C, 73.78; H, 13.93. Found: C, 73.96; H, 13.70.

The phthalic acid ester was prepared as described above for the isomeric alcohol, but on a 2-g. scale. There was obtained a 30% yield of the phthalic acid ester, m.p. 109–110° after recrystallization from chloroform.

Anal. Calcd. for $C_{16}H_{22}O_4$: C, 69.29; H, 7.68. Found: C, 69.01; H, 7.63.

3,4-Dimethyl-3,4-hexanediol.—This was prepared by the "Organic Syntheses"¹³ method for pinacol. On distilling the benzene solution of the reaction mixture obtained from 1316 (15 moles) of ethyl methyl ketone, there was obtained 269 g. (37% yield), b.p. 106–108° at 27 mm., n^{25}_D 1.4520. Reported physical constants:⁴ b.p. 94–95° (10 mm.); n^{20}_D 1.4540. This material was maintained at 20° and seeded with a few crystals of the solid modification of the pinacol, obtained by freezing the material and triturating with ether. After standing three days, 40 g. of the solid modification was removed by filtration. Second and third crops of 6 and 1 g., respectively, were obtained at 3-day intervals. The combined solid fractions were dissolved in ether, cooled overnight at –20° and filtered. There was obtained 30 g. of the *meso*-3,4-dimethyl-3,4-hexanediol, m.p. 52–53°; literature values, 44°, ⁵ 49°, ^{16,7} 51°. ⁸

Anal. Calcd. for $C_8H_{18}O_2$: C, 65.71; H, 12.41. Found: C, 66.16; H, 12.35.

The assignment of the *meso* configuration is based on analogy with the 4,5-octanediols where the form melting at 124° has been demonstrated to be the *meso*-isomer; the *dl*-form melts at 28°. ⁹

The mother liquor from the filtration step was fractionally distilled and 200 g. of the *liquid form* obtained, b.p. 115–116° at 35 mm., n^{25}_D 1.4520. This is assumed to be predominantly the *dl*-form.

Anal. Calcd. for $C_8H_{18}O_2$: C, 65.71; H, 12.41. Found: C, 65.90; H, 12.16.

The reported b.p. is 94–95° at 10 mm.; ⁴ 205–205.7° at 752 mm.; n^{20}_D 1.4540. ⁴

Rearrangement of Pinacols.—This follows the procedure of Nybergh.¹⁴ Eight hundred milliliters of concentrated sulfuric acid was cooled to –10°. To this was added 100 g. of the liquid form of the pinacol over a period of an hour with mechanical stirring, the temperature being kept at –10°. It was maintained at this temperature for 2 hours, then poured into an ice-water mixture, and steam distilled. Forty nine grams of water-insoluble material was obtained, which on fractional distillation gave 15 g. (17% yield) of the mixture of isomeric ketones, b.p. 60–63° at 28 mm., n^{27}_D 1.4185.

Anal. Calcd. for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 75.20; H, 12.28.

Much of the residue consisted of a high boiling fraction, b.p. 249–254° at 760 mm.

Anal. Calcd. for $C_{16}H_{34}$: C, 87.20; H, 12.80; mol. wt., 220. Found: C, 87.15; H, 12.55; mol. wt. (f.p. depression in C_6H_6), 211.

The *meso*-pinacol was rearranged in the same manner but on a 40-g. scale. The only difference observed at this point was that the *meso*-form required about an hour to dissolve in the sulfuric acid whereas the liquid form dissolved immediately. After the steam distillation, 26.5 g. (75% of theory) was obtained which on distillation gave 17.5 g. (50% yield), b.p. 60–61° at 27 mm., n^{25}_D 1.4198 of the mixture of isomeric ketones.

Anal. Calcd. for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 75.27; H, 12.25.

The other material obtained was a small amount of a high boiling liquid which appeared to be identical with the $C_{16}H_{34}$ olefin of the preceding paragraph.

Analysis of the Mixtures of Pinacolones.—A 15-g. sample of each mixture was hydrogenated under the same conditions as described above in the preparation of 3-ethyl-3-methyl-2-pentanol. Data obtained on the mixtures of alcohols are summarized in Table I.

TABLE I
DATA ON THE MIXTURE OF THE ISOMERIC ALCOHOLS

Property	Mixture of alcohols from the <i>meso</i> -pinacol	Mixture of alcohols from the <i>dl</i> -pinacol
B.p. at 28 mm., °C.	78	80
% yield, from ketone	88	74
n^{25}_D	1.4370	1.4370
% C (Th. 73.78)	74.16	74.00
% H (Th. 13.93)	13.79	13.79
M.p. of phthalic acid ester, °C.	102.5–104	103.5–105.5
% 3-Ethyl-3-methyl-2-pentanol from infrared absorption at 8.02 μ	73	70

The infrared spectra of the pure reference alcohols and of the two mixtures of alcohols were first obtained from 6.5 to 12 μ using a Perkin-Elmer single beam instrument with a sodium chloride prism. From the shape of the curves, it was apparent the mixtures consisted mostly of the 3-ethyl-3-methyl-2-pentanol. Mixtures of the reference alcohols in appropriate ratios were then dissolved in 10 times their weight of benzene and their spectra determined from 7.5 to 8.3 μ . The unknown mixtures of alcohols were likewise dissolved in 10 times their weight of benzene, and their spectra determined in this region. Comparisons could be made at 8.02 μ with an accuracy estimated to be within a few per cent.; the results are in Table I.

Acknowledgment.—The authors wish to gratefully acknowledge the assistance of Drs. Robert Spurr and Joseph Wenograd in obtaining and interpreting the infrared spectra.

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(3) R. Adams and E. W. Adams in Gilman and Blatt's, "Organic Syntheses," Coll. Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 459.

(4) L. Schermerling, B. S. Friedman and V. N. Ipatieff, *THIS JOURNAL*, **62**, 2446 (1940).

(5) G. Bernard and J. Cologne, *Bull. soc. chim. France*, [5] **12**, 354 (1945).

(6) N. Zelinsky and S. Krapivin, *Zhur. Russ. Fiz. Khim. Obshchestva*, **24**, 24 (1892), from *J. Chem. Soc.*, **64**, 390 (1893).

(7) J. F. Norris and E. H. Green, *Am. Chem. J.*, **26**, 315 (1901).

(8) E. Pace, *Atti acad. Lincei*, **8**, 309 (1928).

(9) S. Veibel, *Biochem. Z.*, **239**, 456 (1931), from *Brit. Chem. Abstr.*, **A**, 1332 (1931); W. G. Young, L. Levanas and Z. Jasaitis, *THIS JOURNAL*, **58**, 2274 (1936).