

2-Phenyl-1,8-trimethyleneindole.—One gram of the hydrazone of N-aminotetrahydroquinoline and acetophenone was ground in a mortar with 5 g. of powdered anhydrous zinc chloride and the mixture was heated at 120° for one hour. The mass was then warmed with several small quantities of dilute hydrochloric acid to dissolve the zinc chloride. The residual gummy brown precipitate was filtered, dried, powdered and extracted with ether to separate the indole from brown ether-insoluble by-products. The residue obtained on evaporation of the extracts, when recrystallized from 10 cc. of alcohol, yielded 0.2 g. of the indole, m. p. 130–132° (22% yield). After two recrystallizations from alcohol, from which the substance separated as glittering, colorless leaves, it melted at 133–134°.

Anal. Calcd. for $C_{17}H_{15}N$: C, 87.50; H, 6.49; N, 6.01. Found: C, 87.32; H, 6.41; N, 5.91.

The substance gave with Ehrlich's reagent in the cold a violet color which turned blue on standing.

N - Amino-1,2,3,4-tetrahydro-5,6-benzoquinoline.—The necessary N-nitrosotetrahydrobenzoquinoline was prepared by the procedure of Bamberger and Müller.¹³ Yields of 60–70% were obtainable if an adequate quantity of water was used to keep dissolved at 0° the rather insoluble salt of the tetrahydrobenzoquinoline.

The N-aminotetrahydrobenzoquinoline was prepared in yields of 35–40% by mild reduction of the nitroso compound with zinc dust and acetic acid in aqueous alcoholic solution, according to the procedure for N-aminotetrahydroquinoline. The product was isolated as the sulfate, which, after recrystallization from 0.6 N sulfuric acid, separated as glistening brown needles and leaves, m. p. 182° with decomposition.

(13) Bamberger and Müller, *Ber.*, **24**, 2644 (1891).

Anal. Calcd. for $C_{26}H_{30}O_4N_4S \cdot 4H_2O$: N, 9.90. Found: N, 10.15.

Anal. of salt after drying at 120°. Calcd. for $C_{26}H_{30}O_4N_4S$: N, 11.34. Found: N, 11.30, 11.35.

The free base, formed by decomposition of the sulfate in hot aqueous-alcoholic solution with dilute alkali, consisted of tan crystals which melted at 107–108° after two recrystallizations from ligroin.

Anal. Calcd. for $C_{13}H_{14}N_2$: N, 14.18. Found: N, 13.94.

This hydrazine was moderately soluble in alcohol, nearly insoluble in water. It reduced Tollens' solution rapidly in the cold, and Fehling's solution slowly on boiling.

Summary

1. The chemistry of a new tricyclic indole, 1,8-trimethyleneindole, has been studied. The 2-carboxy and 2-phenyl derivatives are also reported, but the 2-methyl derivative could not be obtained. The preparation of the intermediate hydrazones, the pyruvic acid, acetophenone and acetone hydrazones of N-amino-1,2,3,4-tetrahydroquinoline is reported.

2. N-Amino-1,2,3,4-tetrahydro-5,6-benzoquinoline and its pyruvic acid hydrazone have been prepared. The latter is inactive toward indolizing agents.

3. The pyruvic acid hydrazone of N-amino-carbazole is likewise not convertible to an indole.

EDINBURGH, SCOTLAND

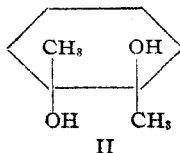
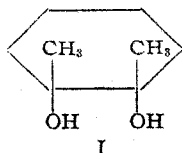
RECEIVED JULY 19, 1938

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Inversion in the Pinacol Rearrangement of 1,2-Dimethylcyclopentenediol-1,2*

BY PAUL D. BARTLETT AND ABRAHAM BAVLEY

It has been pointed out¹ that in the pinacol rearrangement of the geometrical isomers of 1,2-dimethylcyclohexanediol-1,2 (I and II)



the methyl group migrates in preference to the ring carbon atom only in the *cis*-pinacol, in which the methyl group is, on a time average, remote from the hydroxyl which it displaces. Because the cyclohexane ring is non-planar and allows

many different orientations of adjacent substituents with respect to each other, this example leaves something to be desired in exactness of interpretation. For this reason we have investigated the case of *cis*- and *trans*-1,2-dimethylcyclopentenediol-1,2, in which the planar nature of the five-membered ring makes the relative positions of the groups in space much more certain.

The assignment of configurations to the *cis*- and *trans*-isomers is made on the same basis as in the case of the analogous pinacols with six-membered rings. The *cis* isomer, a liquid boiling at 142–146° (20 mm.), is prepared by the action of potassium permanganate in cold aqueous acetone solution on 1,2-dimethylcyclopentene-1. The *trans* isomer, m. p. 99.5–101° (corr.), results

(*) Presented at the Milwaukee meeting of the American Chemical Society, September 6, 1938.

(1) Bartlett and Pöckel, *THIS JOURNAL*, **59**, 820 (1937).

from the hydrolysis of the oxide of the same hydrocarbon. The assignment of configurations is confirmed by the fact that lead tetraacetate reacts more than a thousand times as fast with the "*cis*" as with the "*trans*" isomer, in accordance with the findings of Criegee, Kraft and Rank² for cases where the configuration is in no doubt.

When the *cis* isomer is refluxed with 30% aqueous sulfuric acid, a ketone can be isolated in 87% yield (as semicarbazone) whose physical constants and whose oxime and semicarbazone show it to be identical with the 2,2-dimethylcyclopentanone-1 prepared in different ways by Blanc³ and by Haller and Cornubert.⁴ Thus the methyl group has migrated in that pinacol in which it is in a position to displace the adjacent hydroxyl group by attacking the opposite side of the carbon atom holding it, as in the Walden inversion.

Identical treatment of the *trans* pinacol gives only involatile brown tars, which on standing become progressively more viscous. All our efforts to isolate an unpolymerized product from this reaction have been without avail. Experiments with gentler acid conditions have led to the same type of product, when there was any reaction at all. It seems probable that the pinacol is being dehydrated without rearrangement to yield a dimethylcyclopentadiene which is polymerized irreversibly by any acid strong enough to bring about dehydration. We tried to prove this by carrying out the dehydration in the presence of maleic anhydride and of benzoquinone, but, as might have been anticipated, the diene addition to these reagents was unable to compete with the polymerization reaction under these acid conditions, and again only tar was obtained. An attempt to catch the diene by bromination also failed.

For the interpretation of these reactions it becomes important to know whether this resinification process occurs because the structure and configuration of this pinacol are especially favorable to it, or especially unfavorable to rearrangement, which must be regarded as the normal reaction. To answer this question we carried out some semiquantitative experiments on the reaction rates of the two pinacols when treated under identical conditions with sulfuric acid in

aqueous solution at 52°. Under these conditions, with 0.2 *N* acid, the *cis* pinacol was 53.9% converted in two and one-half hours, while only 24% of the *trans* isomer had disappeared in the same length of time. The actual difference in rate between the two isomers is somewhat greater than appears from these figures; for the *cis* pinacol reacts fast enough with lead tetraacetate to be titrated by this reagent, whereas actual isolation of the *trans* pinacol, with attendant manipulative losses, was the only way we found to follow its reaction. The results are consistent with the view that the constitution of the *trans* pinacol is so unfavorable to rearrangement that here alone the slow simple dehydration takes precedence over the pinacol rearrangement.

The results with the five- and six-membered rings support the generalization that a group cannot migrate in the pinacol rearrangement unless by a simple movement it can reach the adjacent carbon atom on the face opposite to the hydroxyl group which it is replacing. Thus in these pinacols the methyl group can migrate only in the *cis* modifications. In the *trans* form of the six-ring pinacol, ring contraction occurs with much greater ease than in its five-ring analog which by this same reaction would have to yield the strained four-membered ring. Here, therefore, rearrangement is no longer a faster process than dehydration to the allylic alcohol and diene. It seems that under comparable conditions these three modes of reaction of the cyclic pinacols do not differ enormously in the ease with which they occur.

Experimental

Ethyl cyclopentanone-2-carboxylate was prepared by the method of Haller and Cornubert.⁵ Yields from 65 to 70% were obtained, using 200-g. quantities. The product boiled at 114–116° at 20 mm.

Ethyl 2-methylcyclopentanone-2-carboxylate was made according to the directions of the same authors. The yield was 80%, of material boiling at 108.5–112° at 16 mm. pressure, and having n_D^{20} 1.4461.

2-Methylcyclopentanone was prepared by Van Rysselberge's method⁶ which consists of refluxing the keto ester with 4 *N* hydrochloric acid. Yields of 82–86% were obtained. The product boiled at 139–142°, and yielded a semicarbazone melting at 174–174.8°.

1,2-Dimethylcyclopentanol-1 was prepared in 70–73% yield by the action of the methyl Grignard reagent upon 2-methylcyclopentanone. The product boils from 56 to 62.5° under 16 mm. pressure, showing an inhomogeneity which is attributed by Van Rysselberge to the presence of

(2) (a) Criegee, *Ann.*, **481**, 263 (1930); (b) Criegee, Kraft and Rank, *ibid.*, **507**, 159 (1933).

(3) Blanc, *Bull. soc. chim.*, [4] **3**, 780 (1908).

(4) Haller and Cornubert, *Compt. rend.*, **179**, 315 (1924).

(5) Haller and Cornubert, *Bull. soc. chim.*, [4] **39**, 1726 (1926).

(6) Van Rysselberge, *Bull. soc. chim. Belg.*, **35**, 311 (1926).

geometrical isomers. No attempt was made to separate these.

1,2-Dimethylcyclopentene-1 was obtained in 83–87% yield by refluxing 1,2-dimethylcyclopentanol-1 with iodine for ten hours with a water trap in the return, and distilling. The fraction boiling at 102.5–105.8° was collected, d_{20}^{20} , 0.7950.

1,2-Dimethyl-1,2-epoxycyclopentane.—A solution of 38.5 g. of perbenzoic acid in 700 cc. of chloroform was stirred vigorously and cooled to 0°; 23.5 g. of 1,2-dimethylcyclopentene-1 was added over a period of two and one-half hours, the temperature being held at 0°. Stirring was continued for ten hours, the temperature being held at –5°. After standing at +5° for two days, the solution was extracted with 10% sodium hydroxide to remove benzoic acid, washed, dried with sodium sulfate, and distilled; 23 g. of a liquid boiling at 120–122.5° at 20 mm. was obtained, yield 85%.

Anal. Calcd. for $C_7H_{12}O$: C, 75.0; H, 10.7. Found: C, 74.7, 74.9; H, 10.5, 10.7.

trans Pinacol by Hydrolysis of the Epoxide.—Twenty-one grams of the oxide was allowed to drop slowly into 20 cc. of water acidified with 6–8 drops of concentrated sulfuric acid, to which ice was added. On gentle shaking the oxide went into solution. By saturation with potassium carbonate the glycol was salted out of solution as a powdery precipitate. It was taken up in ether, from which it crystallized in long needles melting at 99.5–101° (corr.). The yield was 74% of the theoretical.

Anal. Calcd. for $C_7H_{14}O_2$: C, 65.1; H, 11.6. Found: C, 64.7, 64.9; H, 11.3, 11.6.

cis-1,2-Dimethylcyclopentanediol-1,2 was prepared following a general procedure of Harries.⁷ To a solution of 25 g. of 1,2-dimethylcyclopentene-1 in 50 cc. of acetone, cooled to –5°, a solution of 47 g. of potassium permanganate in 100 cc. of water and 1 liter of acetone was added slowly. After standing for one hour, the manganese dioxide slime was filtered off. Carbon dioxide was passed into the solution until potassium bicarbonate precipitated. From the filtrate, the acetone was removed on the water-bath and by distillation the fraction boiling at 142–146° at 20 mm. was collected. This amounted to 14 g. (45.2% of the theoretical yield) of a colorless liquid.

Anal. Calcd. for $C_7H_{14}O_2$: C, 65.1; H, 11.6. Found: C, 64.8, 64.7; H, 11.5, 11.5.

We were not successful in preparing any esters of this pinacol, but it could be condensed with benzaldehyde in the presence of ammonium sulfate to a solid crystallizing in plates, m. p. 120–122.5° (corr.).

Anal. Calcd. for the acetal, $C_{14}H_{18}O_2$: C, 77.5; H, 8.2. Found: C, 77.0, 77.1; H, 7.9, 8.1.

Rearrangement of the cis Pinacol.—Five grams of the liquid "cis" pinacol was dissolved in 20 cc. of water containing 5 cc. of concentrated sulfuric acid. The solution turned green immediately. After refluxing for three hours a brown oil had appeared, while the aqueous solution was practically colorless. To the steam distillate, semicarbazide hydrochloride and sodium acetate were added, yielding 5.2 g. (87.1%) of crude semicarbazone. In

another run the ketone was isolated directly, distilled through a Widmer column, and the fraction boiling at 142–143.8° was collected. Its semicarbazone, recrystallized from methyl alcohol, melted at 191.5–191.8° (corr.). The oxime melted at 68.7° (corr.). Blanc⁸ reports 142° as the boiling point of 2,2-dimethylcyclopentanone-1, and 69° as the melting point of the oxime. Haller and Cornubert⁹ report the melting point of the semicarbazone as 191°.

Dehydration of the trans Pinacol.—On treatment identical with that applied to the *cis* pinacol, the *trans* isomer yielded no volatile product but, after showing similar color changes, gave a brown tar which rapidly became more viscous on standing and set to an almost black glass. No product which could be characterized was had from attempts to use less dilute acid, to carry out the experiment in acetic anhydride, glacial acetic acid, acetyl chloride, or in the presence of bromine, maleic anhydride, or benzoquinone.

Rates of Reaction with Lead Tetraacetate.—This reagent was prepared by the method of Dimroth⁸ and the titrations with it were carried out according to the directions of Criegee and his co-workers.^{2b} In a thermostat at 25°, the following results were obtained: 0.0595 g. of the *cis* pinacol was put into solution in 9.92 cc. of acetic acid (f. p. 16.2°) which had been refluxed with lead tetraacetate for ten hours and distilled. To this was added 9.92 cc. of a standard solution containing 0.02266 g. of lead tetraacetate per cc. of acetic acid. By iodometric titration the reaction was found to be 98.6% complete after five hours. Thus this reaction can be made the basis of a satisfactory titration method for the *cis* pinacol.

0.0573 g. of the *trans* pinacol was dissolved in 9.92 cc. of acetic acid and added to the same volume of standard lead tetraacetate solution. After seven hours and seven minutes, only 69.7% of the pinacol had reacted. A rough calculation based upon several such runs shows a 1600-fold difference between the rates of reaction of the isomeric pinacols with lead tetraacetate. Evidently the reaction in the case of the *trans* pinacol is too slow to serve as the basis of a titration method for the pinacol.

Rate of Rearrangement of the cis Pinacol.—0.209 g. of *cis* pinacol was dissolved in 10 cc. of water, and 10 cc. of 0.2 *N* sulfuric acid was added. The whole was kept at 52° in the thermostat. After two and one-half hours excess sodium acetate was added and 20.1 cc. of standard lead tetraacetate. This was allowed to stand at 35° for eight hours and the lead tetraacetate was then titrated iodometrically. The rearrangement was 53.9% complete.

Rate of Dehydration of trans Pinacol.—In order to gain an idea of the rate of reaction of the *trans* pinacol with sulfuric acid, it was necessary to resort to isolation of the unchanged *trans* pinacol, since a suitable titration method was not found. 0.210 g. of *trans* pinacol was dissolved in 10 cc. of water and 10 cc. of 0.2 *N* sulfuric acid was added. The reaction was allowed to proceed at 52° for two and a half hours, at the end of which time barium oxide was added, the barium sulfate precipitate digested on the steam-bath overnight, and filtered off. The pinacol was recovered by ether extraction of the filtrate, after concentrating *in vacuo*, and recrystallization from ether of the crude product. 1.6 g. of the pinacol was recovered (76%

(7) Harries, *Ber.*, **34**, 2979 (1901).

(8) Dimroth, *ibid.*, **53**, 483 (1930).

of the starting material) melting at 100.5–100.7° alone and when mixed with the original material.

Summary

1. *cis*-1,2-Dimethylcyclopentanediol-1,2 undergoes the pinacol rearrangement with migration of a methyl group and production of 2,2-dimethylcyclopentanone.

2. *trans*-1,2-Dimethylcyclopentanediol-1,2 when boiled with dilute aqueous acid undergoes resinification. It has not been possible to char-

acterize any product from this reaction. It is suggested that dehydration without rearrangement is here occurring, yielding a product which is rapidly polymerized by the acid.

3. These observations confirm the conclusion previously reached that in the pinacol rearrangement elimination of a hydroxyl group and the arrival of a migrating radical occur on opposite sides of the same carbon atom.

CAMBRIDGE, MASS.

RECEIVED AUGUST 5, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Pyrolysis of Esters

BY CHARLES D. HURD AND FORD H. BLUNCK

Although much is known about the pyrolysis of esters, most of the evidence is fragmentary. To supply additional information of a critical nature seven esters were selected for detailed study. These were ethyl, phenyl, *i*-propyl, *i*-butyl, and *t*-butyl acetates and methyl and ethyl phenylacetates.

The known facts concerning simple esters may be summarized briefly. If a β -H is present in the alkyl portion of the ester, $\text{RCOOCR}_2\text{CHR}_2$, the decomposition into acid (RCOOH) and olefin ($\text{R}_2\text{C}=\text{CR}_2$) is general. This was established by Oppenheim and Precht¹ for ethyl acetate and was confirmed recently by Bilger and Hibbert.² The latter investigators also extended the reaction (470–500°, 1.2 sec. contact time) to several other esters which included not only the propyl, *i*-propyl, *n*-butyl, *i*-butyl, *s*-butyl and β -chloroethyl acetates but also the ethyl esters of benzoic, formic, butyric and chloroacetic acids. In their work an unsuccessful search was made for aldehydes among the reaction products, the reagent being a solution of *p*-nitrophenylhydrazine in acetic acid. Bilger and Hibbert noted that methyl and benzyl esters (of acetic and benzoic acids) did not decompose under conditions which caused breakdown of the other esters.

The decomposition products of methyl phenylacetate (sealed tube at 360°) have been reported³ to be toluene, methane, methanol and oxides of

carbon. Methyl acetate,⁴ at 1100°, has been found to change into acetic acid, formaldehyde and acetaldehyde (or their decomposition products) and ethylene.

Five of the esters studied in the present investigation possessed a β -H on the alkyl group. Greatest instability was noticed when this alkyl was tertiary as in *t*-butyl acetate. It decomposed even at 360°. Secondary alkyl (*i*-propyl acetate) exhibited intermediate stability. Greatest stability was noticed when the alkyl was primary (ethyl or *i*-butyl acetates, ethyl phenylacetate).

Nearly equivalent amounts of acetic acid and isobutylene were observed from *t*-butyl acetate at 360–430° and no other products were found. Also, no products other than ethylene and phenylacetic acid (formed in equivalent amounts) were obtained from ethyl phenylacetate at 435–545°. At 625°, however, the latter gave rise to small amounts of toluene and carbon dioxide which were formed obviously from phenylacetic acid by secondary decomposition. The percentage yields of products based on the ester decomposed were found to be as follows: phenylacetic acid 58, toluene 22, carbon dioxide 21, ethylene 78.

The acetic acid and propylene from *i*-propyl acetate were formed in nearly equimolar amounts, but small amounts of acetaldehyde (4%), acetone (3%) and carbon monoxide (12%) were also observed in an experiment at 460°.

Ethyl acetate yielded acetic acid and ethylene in approximately equivalent amounts as expected, but the presence of other products was established

(1) Oppenheim and Precht, *Ber.*, **9**, 325 (1876); Burns, Jones and Ritchie, *J. Chem. Soc.*, 400 (1935).

(2) Bilger and Hibbert, *THIS JOURNAL*, **58**, 823 (1936).

(3) Engler and Löw, *Ber.*, **26**, 1440 (1893).

(4) Peytral, *Bull. soc. chim.*, **31**, 118 (1922).