Upon heating to 190° it decomposed to give one equivalent of carbon dioxide. The compound was not investigated further and was assumed to be XII. The benzene layer was evaporated to dryness and the residue fractionally sublimed. The first fraction was apparently benzaldehyde, but a second fraction, subliming at 150° at 25 mm. pressure was a yellow crystalline solid, which melted at 62–63°, after resublimation.

Anal. Calcd. for $C_{14}H_{11}NO_2$: C, 74.80; H, 4.93; N, 6.23. Found: C, 75.00; H, 5.19; N, 6.44.

The oxime of this compound melted at 205–207°. Beckmann and Köster have reported a m. p. of 63° for phenylglyoxylanilide and a m. p. of 205–206° for the oxime.[6] A similar oxidation of 1,4-diphenyl-2-*p*-chlorobenzylidene-3,5-pyrrolidione also gave phenylglyoxylic acid anilide.

1,4-Diphenyl-2-*p*-chlorobenzylidene-3,5-pyrrolidione (IXa, Xa).—These compounds were prepared similarly to the unchlorinated compounds IX and X. IXa melted at 196–199°. Xa melted at 200–205°.

Anal. Calcd. for $C_{23}H_{16}ClNO_2$: Cl, 9.49. Found: Cl, 9.40.

Anal. Calcd. for $C_{23}H_{16}ClNO_2$: Cl, 9.49. Found: Cl, 9.64.

A mixed melting point of IXa and Xa was 196–204°; however, the infrared spectra of the compounds showed marked differences and thus proved their dissimilarity.

Summary

The condensation of N-phenacetyl-N-phenylglycine with benzaldehyde or with *p*-chlorobenzaldehyde in the presence of acetic anhydride has been shown to give geometric isomers of the expected oxazolidones.

Each of the oxazolidones have been isomerized to a mixture of the two forms.

The isomeric oxazolidones have been rearranged upon treatment with a sodium alcoholate to isomeric pyrrolidiones.

New Brunswick, N. J. Received March 20, 1950

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[6] Beckmann and Köster, *Ann.*, **274**, 9 (1893).

[Contribution from the Department of Chemistry, University of Delaware]

The Oxidation of Benzpinacolyl Alcohol

By William A. Mosher and Howard A. Neidig[1]

Recent reports from this laboratory have indicated the generality of the cleavage of aliphatic secondary alcohols on oxidation with chromic anhydride.[2] Concurrent with studies of aliphatic compounds, oxidation of analogous aromatic structures has been underway. Benzpinacolyl alcohol (phenyltriphenylmethylcarbinol) is analogous to methyl-*t*-butylcarbinol, one of the first examples of the cleavage reaction. On oxidation with chromic anhydride, in 70% aqueous acetic acid, this compound yielded 61% benzopinacolone, 22% triphenylcarbinol, 7% tetraphenylethylene and 6% benzaldehyde, all calculated on a molar basis. Benzoic acid has been obtained in some runs in amounts closely equivalent to triphenylcarbinol. The 22% cleavage here obtained is in contrast to a maximum of 7% found with methyl-*t*-amylcarbinol.[2]

Delacre[3] found that benzpinacolyl alcohol could be cleaved by alkali in high yield to triphenylmethane and benzaldehyde. Triphenylmethane is readily oxidized to triphenylcarbinol so that additional evidence was necessary to determine whether the cleavage reaction was entirely oxidative or caused by some other mechanism followed by oxidation. Identical oxidative conditions with triphenylmethane gave only 34% oxidation. A competitive reaction using equimolar amounts of benzpinacolyl alcohol and triphenylmethane was carried out: 88% of the triphenylmethane was recovered and a 50% yield of benzopinacolone was obtained, comparable with 61% when the secondary alcohol was oxidized alone. Under similar conditions the ketone benzopinacolone did not oxidize. It would appear that the cleavage is a direct result of oxidative attack on the secondary alcohol.

Other oxidizing agents have been studied. Potassium permanganate in acetic acid gave 54% triphenylcarbinol and 57% benzaldehyde. Potassium permanganate in boiling acetic acid gave no oxidation with benzopinacolone and gave a 57% yield of benzophenone with triphenylmethane. No benzophenone was found in the oxidation of benzpinacolyl alcohol. Neutral permanganate in acetone gave no oxidation of benzpinacolyl alcohol whereas oxidation was rapid in acetone containing acetic acid even at 40°. This may be a significant fact in elucidating the mechanism of permanganate oxidations.

Selenium dioxide in acetic acid was without effect on benzpinacolyl alcohol at 70° or 100°.

Lead tetraacetate has been postulated as oxidizing through a free radical mechanism[4] and to be rather specific for 1,2-glycols and related compounds.[5] At 50° this agent gave 70% triphenylcarbinol and 4% tetraphenylethylene; at 120°, where more free radical type reactions should be apparent, the products were 51% tetraphenylethylene, 35% benzaldehyde, and 33% triphenylcarbinol. The same reaction was repeated in the presence of air. Had any tri-

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[1] From a thesis submitted by Howard A. Neidig in partial fulfillment of the requirements for the degree of Doctor of Philosophy, University of Delaware, September, 1948. Complete experimental details may be obtained from this thesis.

[2] Mosher, This Journal, **70**, 2544 (1948); **71**, 286 (1949).

[3] Delacre, *Bull. Acad. Roy. Belgique*, [3] **20**, 109 (1890).

[4] *Cf.* Waters, "The Chemistry of Free Radicals," second edition, Oxford Press, New York, N. Y., 1948, p. 227 *et seq.*

[5] *Cf.* Baer, This Journal, **64**, 1416 (1942), for references to recent studies.

phenylmethyl free radical been present, it should have reacted to give the very stable triphenylmethyl peroxide. This compound was not found. This peroxide is stable to oxidation with lead tetracetate under similar conditions. We believe this excludes the cleavage reaction proceeding through a free radical mechanism.

The retropinacolone rearrangement brought about by lead tetraacetate was entirely unexpected. Acetic acid alone or containing lead acetate, the end product of lead tetraacetate oxidations, did not cause this rearrangement. Either lead tetraacetate in acetic acid solution has an unexpected acidity or we have an example of the electrophilic nature of an oxidizing agent bringing about acid catalyzed dehydration, also an electrophilic attack. This situation is receiving further study.

Our proposed mechanism involves attack of the oxidizing reagent on the hydrogen of the hydroxyl group. Westheimer[6] has shown that in the oxidation of isopropyl alcohol with chromic anhydride the breaking of the C–H bond on the secondary carbon is involved in the rate determining step. We have previously considered attack on this hydrogen for historical reasons but abandoned it because it could not give a simple explanation of the cleavage reactions referred to above. We considered a point of electronic deficiency *beta* to the observed points of cleavage to be essential and therefore have favored direct attack on the hydroxyl hydrogen. Westheimer's work[6] establishes clearly a difference in reactivity of C–H bonds as compared with C–D bonds. The energy required to break any bond should be essentially the same regardless of the method of rupture, whether it is due to an expulsion of an ion or whether it is due to the pulling off of an ion by an outside agent. However, the possibility of chromate ester formation with subsequent decomposition, as more recently suggested by Westheimer,[7] is certainly not excluded. The oxidation of secondary ethers presented itself as a means of giving further information on the point of attack of oxidizing agents. So far, however, attempts to prepare ethers of benzpinacolyl alcohol have been negative; alkaline conditions of etherification gave over 90% triphenylmethane whereas methods involving acid conditions lead to the retrobenzopinacolone rearrangement and 90% tetraphenylethylene is recovered. Diazomethane, uncatalyzed and catalyzed with aluminum isopropoxide, gave no reaction. The reagent oxidation of various ethers is under active investigation at the present time.

We wish to thank the Research Corporation for a Frederic Cottrell Grant which made this work possible.

Experimental

General.—Benzpinacolyl alcohol was prepared by the Grignard reduction[8] of benzopinacolone, prepared by the methods in "Organic Syntheses."[9] Identification of all products was by means of mixed melting points of both compound and a solid derivative.

Competitive Oxidation of Triphenylmethane and Benzpinacolyl Alcohol.—To 5 g. of benzpinacolyl alcohol (0.014 mole) and 3.4 g. of triphenylmethane (0.014 mole) dissolved in 300 ml. of glacial acetic acid was added 0.95 g. of chromic acid (0.009 mole) dissolved in acetic acid at a temperature of 60–65°. Upon cooling, 2.3 g. (47%) benzopinacolone crystallized out. From the filtrate, 3.0 g. (85.3%) triphenylmethane and traces of triphenylcarbinol were isolated.

Oxidations of Benzpinacolyl Alcohol. Chromic Acid.—To 24 g. (0.073 mole) dissolved in 125 ml. of acetic acid, 4.8 g. of chromic anhydride (0.048 mole) dissolved in acetic acid and water was added in one hour at a temperature of 64°; 14.3 g. (61.3%) of benzopinacolone was obtained on filtering the reaction mixture. In addition, 4.2 g. (22.2%) of triphenylcarbinol was obtained. On the steam distillation of the reaction mixture, 0.7 g. (6%) of benzaldehyde was obtained. Extraction of the reaction mixture gave 1.5 g. (6.6%) of tetraphenylethylene.

Potassium Permanganate in Acetic Acid.—To 10 g. (0.028 mole) dissolved in 300 ml. of glacial acetic acid, 1.7 g. of potassium permanganate (0.11 mole) dissolved in a mixture of acetic acid and water was added at a temperature of 60–64°; time, three hours. To the reaction mixture was added 2,4-dinitrophenylhydrazine, and the resulting precipitate filtered and purified; 5.5 g. (56.7%) of the 2,4-dinitrophenylhydrazone of benzaldehyde was obtained. By pouring the filtrate into water, a precipitate formed from which 4 g. (54%) of triphenylcarbinol was isolated.

Potassium Permanganate in Acetone.—To 5.5 g. (0.015 mole) dissolved in 100 ml. of acetone, 400 ml. of acetone containing 1 g. of potassium permanganate (0.007 mole) was added at reflux; time, one and one-half hours. Removal of the excess solvent gave 5.4 g. (98%) of benzpinacolyl alcohol.

Selenium Dioxide in Acetic Acid.—To 5 g. (0.014 mole) dissolved in 300 ml. of glacial acetic acid was added 1 g. of selenium dioxide (0.009 mole) dissolved in acetic acid and water at a temperature of 61–63°; time, two hours. The reaction mixture was poured into an equal volume of water, and the resulting precipitate was 4.7 g. (94%) of benzpinacolyl alcohol and 0.1 g. of unidentified tar.

Lead Tetraacetate in Acetic Acid.—Run No. 1: to 5 g. (0.014 mole) dissolved in glacial acetic acid, 4 g. of lead tetraacetate (0.009 mole) in acetic acid and acetic anhydride was added at a temperature of 50°; time, three hours. The reaction mixture was poured into water, and fractional crystallization of the resulting precipitate gave (I) 2.6 g. (70.2%) triphenylcarbinol, (II) 0.2 g. (4.2%) tetraphenylethylene. Run No. 2: To 10 g. (0.028 mole) in glacial acetic acid (300 ml.) and acetic anhydride (20 ml.), 14.1 g. of lead tetraacetate (0.031 mole) dissolved in 50 ml. acetic acid and 50 ml. acetic anhydride was added at reflux (120°); time, two hours. Addition of petroleum ether to the reaction mixture gave both tetraphenylethylene and benzpinacolyl acetate. When an equal volume of water was added to the filtrate, an oil was obtained from the petroleum ether layer which upon extraction with chloroform and carbon tetrachloride mixture gave tetraphenylethylene, triphenylcarbinol, and benzaldehyde; 2.4 g. (32%) of triphenylcarbinol, 4.8 g. (51%) of tetraphenylethylene, and 1.05 g. (35%) of benzaldehyde were obtained.

Reactions of Benzpinacolyl Alcohol. Thionyl Chloride in Chlorobenzene.—To 30 g. (0.086 mole) dissolved in chlorobenzene was added 10 ml. of thionyl chloride (0.14 mole) and refluxed for sixty-four hours. After distilling

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(6) Westheimer, THIS JOURNAL, **71**, 25 (1949).

(7) Before Symposium on Organic Reaction Mechanisms, Gordon Research Conferences, AAAS, New London, N. H., 1948.

(8) W. E. Bachmann, THIS JOURNAL, **55**, 3857 (1933).

(9) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, New York, N. Y., 1943, pp. 71, 73.

the excess solvent, 25 g. (88%) of tetraphenylethylene was isolated.

Alcoholic Potassium Hydroxide.—To a warm solution of 10 g. of potassium hydroxide in 90 g. of ethyl alcohol was added 2 g. of benzpinacolyl alcohol (0.006 mole) and refluxed for four hours. The reaction mixture was poured into water and extracted with benzene. From the benzene extraction, 1.30 g. (93%) of triphenylmethane and a small amount of benzaldehyde were isolated.

Diazomethane in Ether.—Run No. 1: to an ethereal solution of diazomethane prepared by adding 20 g. of powdered nitrosomethyl urea in small portions to 200 ml. of ether and 60 ml. of 40% potassium hydroxide, was added 17 g. of benzpinacolyl alcohol (0.048 mole) dissolved in 500 ml. of ether at a temperature of 0–5°. The reaction mixture was then heated for forty-three hours. After distilling the excess solvent, 16 g. (94%) of benzpinacolyl alcohol, and traces of triphenylmethane, were obtained. Run No. 2: 10 g. (0.028 mole) and 1 g. of aluminum isopropoxide dissolved in 200 ml. of ethyl ether were added to an ethereal solution of diazomethane prepared as indicated in Run No. 1. The temperature was maintained at 0–5° during addition, and the reaction mixture was then refluxed for eighteen hours. The excess solvent was distilled giving 9.2 g. (92%) of benzpinacolyl alcohol. **Glacial Acetic Acid.**—25 g. (0.071 mole) was heated in 200 ml. of glacial acetic acid at 60–67° for one hour. After distillation of the excess acetic acid, 24.6 g. (94.4%) of benzpinacolyl alcohol was recovered. **Lead Acetate and Acetic Acid.**—5 g. (0.014 mole) was heated with 1 g. of lead acetate in 300 ml. of glacial acetic acid for two hours. From the precipitate formed when the reaction mixture was poured into water, 4.2 g. (84%) of benzpinacolyl alcohol and 0.1 g. (2.5%) of tetraphenylethylene were obtained. **Acetic Anhydride.**—20 g. (0.056 mole) was refluxed with 300 ml. of acetic anhydride for eight hours. After distillation of the excess acetic acid, 19.4 g. (97%) of benzpinacolyl alcohol was recovered. **Metallic Sodium in Benzene.**—To 2 g. (0.006 mole) dissolved in 300 ml. of benzene, 0.3 g. of sodium (0.013 gram atom) was added and refluxed for sixteen hours. The reaction mixture was separated from the unreacted sodium, and 0.61 g. of ethyl bromide was added and refluxed for three hours. The excess solvent was distilled off and 1.3 g. of triphenylmethane (94%) and a trace of benzaldehyde were found.

Summary

1. Oxidation of benzpinacolyl alcohol with chromic anhydride gives 61% benzopinacolone, 22% triphenylcarbinol, 7% tetraphenylethylene, and 6% benzaldehyde. Permanganate in acetic acid gave 54% triphenylcarbinol and 57% benzaldehyde. Permanganate in neutral solution or selenium dioxide did not oxidize the alcohol.

2. Lead tetraacetate gave 70% triphenylcarbinol and 4% tetraphenylethylene at 50° and 51% tetraphenylethylene, 33% triphenylcarbinol and 35% benzaldehyde at 120°. The lower yield of cleavage at elevated temperatures argues against a free radical intermediate as does the absence of triphenylmethyl peroxide when the reaction is carried out in the presence of air.

3. Attempts to prepare ethers of benzpinacolyl alcohol have been unsuccessful.

NEWARK, DELAWARE RECEIVED DECEMBER 2, 1949

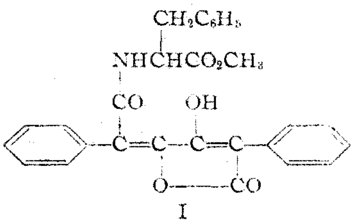
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Structures and Syntheses of Rhizocarpic Acid and Epanorin[1]

BY ROBERT L. FRANK, S. MARK COHEN AND JAMES N. COKER

Rhizocarpic acid is a yellow pigment isolated in 1844 by Knop[2] from a number of lichens and obtained by Zopf[3] in 1895 from the lichen *Rhizocarpon geographicum*. Epanorin is a similar pigment, first found by Zopf in the lichen *Epanora lecanora*.[4] These are the only known nitrogen-containing lichen pigments.

In this paper are described the structure elucidations, confirmed by synthesis, of these two pigments. Rhizocarpic acid (I) is the amide of pulvinic acid with the methyl ester of L-phenylalanine; epanorin (II) is the corresponding derivative of L-leucine.[5]



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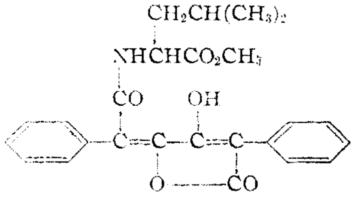

II

Zopf[3,6] reported a molecular formula of $C_{26}H_{20}O_6$ for rhizocarpic acid; Hesse[7] favored the formula $C_{28}H_{22}O_7$. Neither of these authors, however, recognized the presence of nitrogen in rhizocarpic acid, an understandable oversight since no lichen pigments were then known to contain this element.

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(1) This is the third communication on the chemistry of fungi and lichens. For the first two see THIS JOURNAL, **72**, 1824, 1827 (1950).

(2) Knop, *Ann.*, **49**, 122 (1844).

(3) Zopf, *ibid.*, **284**, 107 (1895).

(4) Zopf, *ibid.*, **313**, 330 (1900).

(5) The pulvinic acid derivatives represented in this paper are formulated in the enolic form in accord with previously published structures (see Karrer, Gehrckens and Heuss, *Helv. Chim. Acta*, **9**, 446 (1926)). It is understood that they may actually have the keto form; infrared absorption spectra indicate this may be the case (see reference 12).

(6) Zopf, *Ann.*, **338**, 35 (1905).

(7) (a) Hesse, *Ber.*, **31**, 663 (1898); (b) *J. prakt. Chem.*, [2] **58**, 465 (1898); (c) *ibid.*, **76**, 1 (1907).