By a similar procedure the product of the action of acetylene on ethyl alcohol, without the separation of the acetal, was converted into chloral. The best yield, about 70%, was obtained by chlorination at a temperature of 60° to 80°.

Summary

1. Dimethyl acetal and diethyl acetal were prepared by passing acetylene into the corresponding alcohol in the presence of concd. sulfuric acid and mercuric sulfate.
2. In the presence of the higher alcohols the acetylene is converted largely into the condensation products of acetaldehyde, other than the corresponding acetals.
3. The rate of absorption of acetylene by the alcohol, acid and catalyst mixture decreases with an increasing molecular weight of the alcohol. It is also more rapid in the case of the normal alcohols than in the case of the secondary alcohols.
4. The rate of absorption of acetylene by the mixture of alcohol, acid and catalyst is proportional to the amount of the catalyst used.
5. The products of the partial and complete bromination of dimethyl acetal and the chlorination of dimethyl and diethyl acetal have been determined.
6. A successful method for the preparation of chloral from acetylene has been developed.

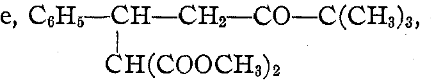
Notre Dame, Indiana

[Contribution from the Department of Chemistry, Wesleyan University]

REDUCTION PRODUCTS OF BENZALPINACOLINE

By G. A. Hill, C. S. Spear and J. S. Lachowicz

Received April 3, 1923

In the course of an investigation of dimethyl β-phenyl-γ-trimethylacetyl ethyl malonate,  $C_6H_5\text{—}\underset{\displaystyle CH(COOCH_3)_2}{\underset{|}{CH}}\text{—}CH_2\text{—}CO\text{—}C(CH_3)_3$, carried on by one of us[1] certain new compounds were obtained which were thought to be reduction products of benzalpinacoline. This surmise was shown to be well founded, for the same substances were later prepared by subjecting benzalpinacoline to the action of aluminum amalgam. At the time, however, no attempt was made to identify them further, or to determine their structures.

As a typical α,β unsaturated ketone, and consequently one possessing the conjugated system, —CH=CH—C=O, benzalpinacoline would be expected[2] to yield with reducing agents, a saturated ketone, A, a saturated

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[1] E. P. Kohler and G. A. Hill; results not yet published.

[2] Thiele, *Ann.*, **306**, 87 (1899).

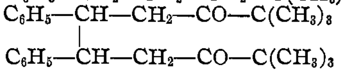
secondary alcohol, B, and possibly a hydrocarbon, C, and a dimolecular product, D.

A. $C_6H_5—CH_2—CH_2—CO—C(CH_3)_3$

B. $C_6H_5—CH_2—CH_2—CHOH—C(CH_3)_3$

C. $C_6H_5—CH_2—CH_2—CH_2—C(CH_3)_3$

D.



$$\begin{array}{l} C_6H_5—CH—CH_2—CO—C(CH_3)_3 \\ \quad\quad\;\; | \\ C_6H_5—CH—CH_2—CO—C(CH_3)_3 \end{array}$$

Three compounds, (1) a high-boiling liquid, A, ω-benzylpinacoline, (2) a solid melting at 142° and presumably, B, β-phenylethyl-*tert*-butyl carbinol, and (3), D, 2,2,9,9-tetramethyl-5,6-diphenyl-decandione-3,8, melting at 208.5°, have been isolated. The other substance, C, trimethyl-γ-phenylpropyl methane, was not found.

The benzalpinacoline for this investigation was made by a modification of Vorländer's method,[3] by condensing benzaldehyde with pinacoline. The latter was produced by a slight alteration in the usual procedure,[4] by the action of dil. sulfuric acid on pinacone hydrate which had been prepared by a method recently developed by Adams.[5]

The reducing agents used in this work were, in the main, metal combinations including aluminum amalgam, magnesium amalgam, sodium amalgam, sodium and ethyl alcohol, sodium and moist ether, and zinc and acetic acid. A catalytic reduction with palladium was also carried out.

In most of the experiments all 3 of the above-mentioned products were obtained, in various amounts, and owing to the extreme insolubility of the dimolecular compound its isolation was made uniformly easy. The liquid substance, the only product of catalytic reduction, was generally found, though not always in sufficient amounts to permit its purification, while the solid melting at 142° was the most difficult to prepare in quantity.

The fact that the liquid was the only substance obtained by catalytic reduction is alone almost enough to establish its structure, for it has been found by Skita[6] and others[7] that an α,β unsaturated ketone is, in the main, reduced to the corresponding saturated ketone by the catalytic method if operated at low pressures. Furthermore the substance, which was only slowly attacked by permanganate, yielded a crystalline derivative with hydroxylamine. Despite the probability that these facts do suffice to prove that this compound is ω-benzylpinacoline, an independent synthesis was successfully undertaken and removed all doubt. Pinacoline was treated with sodamide in the manner suggested by Haller[8] and the metallic derivative allowed to react with benzyl chloride. A compound resulted which,

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[3] Vorländer and Kalkow, *Ber.*, **30**, 2269 (1897).

[4] Fittig, *Ann.*, **114**, 57 (1860).

[5] Adams, *Univ. Illinois Bull.*, **18**, No. 6, p. 41 (1920).

[6] Skita, *Ber.*, **41**, 2938 (1908).

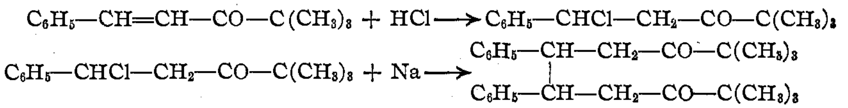
[7] Cornubert, *Compt. rend.*, **159**, 78 (1914).

[8] Haller and Bauer, *Ann. chim.*, [8] **29**, 313 (1913).

by its physical properties and by a mixed melting point determination of its oxime, was shown to be identical with that obtained earlier.

The substance melting at 142° is believed to be β-phenylethyl-*tert*-butyl carbinol, the secondary alcohol which would result from the further reduction of ω-benzylpinacoline, but attempts to prepare it by this and other methods have been unsuccessful. Nevertheless, the determination of its molecular weight and analyses confirm the previously stated supposition as to its nature. Experiments to establish the structure of this compound will be continued in this Laboratory.

The proof that the dimolecular reduction product melting at 208.5° is 2,2,9,9-tetramethyl-5,6-diphenyl-decandione-3,8, was obtained by preparing 1-chloro-1-phenyl-4,4-dimethyl-pentanone-3, following the procedure recommended by Vorländer,[9] and treating this with sodium. The identity of the compound thus produced with that prepared by reduction was established by a mixed melting-point determination.



$$C_6H_5—CH{=}CH—CO—C(CH_3)_3 + HCl \longrightarrow C_6H_5—CHCl—CH_2—CO—C(CH_3)_3$$

$$C_6H_5—CHCl—CH_2—CO—C(CH_3)_3 + Na \longrightarrow \begin{array}{l} C_6H_5—CH—CH_2—CO—C(CH_3)_3 \\ \qquad\quad | \\ C_6H_5—CH—CH_2—CO—C(CH_3)_3 \end{array}$$

Experimental Part

Pinacone hydrate.—This was made according to the method of Adams.[6]

Pinacoline.—A mixture of 250 g. of pinacone hydrate and 750 g. of 6 *N* sulfuric acid was distilled, whereupon crude pinacoline collected in the distillate as a colorless supernatant layer. This was separated, the ketone dried with calcium chloride and fractionated. The fraction boiling at 103–108° was collected separately and amounted to 74 g.; yield, 71.8%.

It was found that the same acid, together with enough water to maintain the original dilution, could be used repeatedly and some time saved by this adaptation of the Richard and Langlais method.[10]

Benzalpinacoline.—A mixture of 100 g. of pinacoline, 120 g. of benzaldehyde (10% excess), 380 cc. of 95% ethyl alcohol, 130 cc. of water, and 100 cc. of 10% sodium hydroxide solution was mechanically shaken in a 1.5 liter bottle for 3 days, then diluted with an equal volume of water, and extracted with benzene. After numerous washings the solution was dried with calcium chloride. Following the removal of the benzene the residue was twice distilled in a vacuum; b. p.$_{10\ \mathrm{mm.}}$, 144–145°; yield, 174 g., or 92.6%. The nearly colorless product was carefully crystallized from ethyl alcohol and yielded practically white crystals; m. p., 43°.

The Reduction of Benzalpinacoline

Action of Aluminum Amalgam.—Five g. of benzalpinacoline was dissolved in 30 cc. of ether, and 2 g. of aluminum amalgam[11] and a few drops of water were added. The reaction mixture, after 2 days during which more water was added, was treated with hydrochloric acid in slight excess. A white precipitate insoluble in ether and the aque-

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[9] Vorländer and Mumme, *Ber.*, **36**, 1480 (1903).

[10] Richard and Langlais, *Bull. soc. chim.*, [4] **7**, 459 (1910).

[11] Weyl, "Methoden der Organischen Chemie," Georg Thieme, Leipzig, **1911**, p. 151.

ous layer separated; m. p., 208.5°. The ethereal layer on evaporation yielded a fine, white crystalline material; m. p., 142°. A little benzalpinacoline was recovered.

Action of Magnesium Amalgam.—Five g. of benzalpinacoline was dissolved in 80 cc. of ether and 11 g. of magnesium amalgam[12] added. The addition of water caused a vigorous reaction, and the resultant magnesium hydroxide precipitate was dissolved by acetic acid; yield, 3.6 g., or 72%; m. p., 208.5°. Some benzalpinacoline was recovered.

Action of Sodium Amalgam.—A solution of 25 g. of benzalpinacoline in 1 liter of alcohol was treated with 435 g. of 2.5% sodium amalgam. The slow addition of 5% sulfuric acid caused the gradual decomposition of the amalgam. After removal of the alcohol the residue was taken up in ether, washed with water, and the ether dried with calcium chloride and distilled. The residue was repeatedly fractionated and yielded the saturated ketone; b. p. $_{\text{atm.}}$, 247°. The weight of the product was not ascertained.

Action of Sodium and Ethyl Alcohol.—(a)[13] To a solution of 5 g. of benzalpinacoline in 50 cc. of absolute ethyl alcohol was gradually added 2.5 g. of sodium. When the reaction ceased, the contents of the flask were diluted with an excess of weak hydrochloric acid, the salt was filtered out and the solution concentrated to ½ its original volume. An oil separated which was taken up in ether. After drying with sodium sulfate, and removal of the solvent, it boiled at 247°; yield, 3.7 g., or 73%.

(b) To a warmed solution of 5 g. of benzalpinacoline in 50 cc. of absolute ethyl alcohol was gradually added 4 g. of sodium. The alcoholate was decomposed with dil. hydrochloric acid, and the solution diluted with thrice its volume of water; an oil of and crystals separated. These were removed with ether, the ethereal solution dried and distilled, and residual semisolid mass pressed on a clay plate, which absorbed the liquid portion of the product; yield, 0.44 g., or 8.6%; m. p., 142°.

Action of Sodium on Moist Ether.[13]—A solution of 5 g. of benzalpinacoline in 50 cc. of ether was floated on 100 cc. of water in a flask attached to a reflux condenser. Carbon dioxide was led into the space above the solution to minimize the danger of fire and explosion; 3.5 g. of sodium was gradually added. At the end of the reaction white crystals were seen at the liquid interface, filtered out and found to melt at 208°. The aqueous layer was extracted with ether and all the ether solutions were dried with sodium sulfate. After removal of the ether 3 g. of the liquid boiling at 247° was obtained; yield, 59%. A further small quantity of the substance melting at 208° was isolated from the residue in the distilling flask; yield, approximately 0.9 g., or 18%.

Action of Zinc and Acetic Acid.—A mixture of 1 g. of benzalpinacoline, 9 g. of zinc turnings, 8 g. of glacial acetic acid and 2 g. of water was warmed for 1 hour on a water-bath. The liquid, containing white crystals, was decanted from the unused zinc and filtered; yield, 0.4 g., or 39%; m. p., 208°. From the filtrate a small quantity of benzalpinacoline was recovered.

Action of Palladium and Hydrogen.—To a solution of 25 g. of benzalpinacoline in 50 cc. of absolute ethyl alcohol were added 1 g. of palladium black and hydrogen from a Kipp generator for several days, until no more was absorbed. The apparatus was shaken constantly during this period. After removal of the alcohol the residue was twice distilled in a vacuum and boiled sharply at 153° at 40–42 mm.; yield, 21.5 g., or 85%.

The Liquid Reduction Product

Properties.—This compound, ω-benzylpinacoline, was obtained as a fragrant, nearly colorless, highly refractive liquid. It boiled at atmospheric pressure at 247° but was more conveniently isolated by distillation under diminished pressure, boiling

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[12] Evans and Fetsch, THIS JOURNAL, **26**, 1158 (1904).

[13] This experiment was performed by Mr. H. D. Hughes, of this University.

at 153° at 40–42 mm. It was slowly attacked by permanganate. With hydroxylamine it yielded a crystalline oxime melting at 95°.

Analyses. Subs., 0.1698, 0.1905; CO_2, 0.5105, 0.5721; H_2O, 0.1443, 0.1579. Calc. for $C_{13}H_{18}O$: C, 82.11; H, 9.47. Found: C, 81.99, 81.89; H, 9.54, 9.29.

Preparation of the Oxime.—To a solution of 0.2 g. of the ketone in 20 cc. of ethyl alcohol 1 g. of hydroxylamine hydrochloride was added. This was decomposed by the calculated amount of potassium hydroxide, the precipitated potassium chloride removed by filtration, and the oxime obtained pure as fine white crystals by evaporation and subsequent recrystallization from alcohol; m. p., 95°.

Analysis. Subs., 0.4073: (Kjeldahl) 49.27 cc. of 0.0403 *N* HCl. Calc. for $C_{13}H_{19}ON$: N, 6.83. Found: N, 6.82.

Synthesis of the Ketone.—Forty g. of finely pulverized sodamide was placed in a 1-liter 3-necked flask, provided with a condenser, a mechanical stirrer, and a separatory funnel, and a solution of 100 g. of pinacoline, in thrice its volume of absolute alcohol-free ether was slowly introduced. This required 2.5 hours as the reaction was fairly vigorous. To complete it the flask contents were refluxed, with continual stirring for 3.5 hours longer. Some sodamide was apparently unattacked. To the yellow solution 126 g. of pure benzyl chloride was slowly added, and the stirring and refluxing continued for 17 hours; 250 cc. of water was added to the reaction mixture and produced a clear, 2-phase liquid system. The ethereal layer was separated, washed with very dil. hydrochloric acid, then with water and dried with calcium chloride. The residue obtained after removal of the ether was fractionated a number of times under reduced pressure; yield, 64 g., or 30%; b. p.$_{43\text{ mm.}}$ 155°. Proof of the identity of this material with that obtained from benzalpinacoline was procured by preparing the oxime in the manner described above, and by running a mixed melting point determination with the oximes. Each melted separately at 95°, and the mixture melted at the same temperature.

The Substance Melting at 142°

Properties.—This compound, presumably β-phenylethyl-*tert*-butyl carbinol, is a white, finely crystalline substance, only somewhat soluble in alcohol, ether or benzene. By the ebullioscopic method, using benzene as a solvent, the average of 3 molecular weight determinations was 181; that calculated is 192. This indicated that this compound is a monomolecular reduction product. Attempts to prepare an acetyl and a benzoyl derivative were unsuccessful, apparently because of the insolubility of the compound.

Analyses. Subs., 0.1384, 0.1424: CO_2, 0.4111, 0.4233; H_2O, 0.1358, 0.1299. Calc. for $C_{13}H_{20}O$: C, 81.25; H, 10.42. Found: C, 81.01, 81.07; H, 10.99, 10.23.

Synthesis.—A number of unsuccessful attempts to synthesize this substance were carried out, but will not be recounted here as work along this line is still in progress.

The Substance Melting at 208.5°

Properties.—This substance, 2,2,9,9-tetramethyl-5,6-diphenyl-decandione-3,8, is a finely crystalline, white compound characterized by its insolubility in the common organic solvents. By the ebullioscopic method using benzene, its molecular weight was found by 3 determinations to be 356; that calculated is 378. This marked it as a dimolecular reduction product of benzalpinacoline. Because of its insolubility, and probably because of steric hindrance, attempts to prepare an oxime or a phenylhydrazone were not successful.

Analyses. Subs., 0.1439, 0.1361, 0.1367, 0.1634: CO_2, 0.4340, 0.4090, 0.4109, 0.4907; H_2O, 0.1216, 0.1121, 0.1138, 0.1349. Calc. for $C_{26}H_{34}O_2$: C, 82.54, H, 8.99. Found: C, 82.26, 81.96, 81.98, 81.90; H, 9.47, 9.23, 9.33, 9.26.

Synthesis.—A solution of 5 g. of benzalpinacoline in 50 cc. of absolute ether was saturated with hydrogen chloride. By evaporation of the ether in a vacuum at room temperature, a white residue of 1-chloro-1-phenyl-4,4-dimethyl-pentanone-3 resulted. This somewhat unstable substance, without further purification, was dissolved in 50 cc. of absolute ether and treated with 0.8 g. of sodium wire chips. After the reaction moderated the flask contents were refluxed and intermittently shaken for an hour, and then allowed to stand for 12 hours. A white precipitate of sodium chloride appeared. The excess of sodium was carefully removed and 50 cc. of water added. No evolution of gas was observed, the salt dissolved and white crystals collected at the liquid interface. These were separated and another small amount was later deposited from the ether layer; yield, 0.4 g., or 7.9%. Some benzalpinacoline was recovered. The product thus prepared melted alone at 208.5°, the dimolecular reduction product of benzalpinacoline behaved similarly, and a mixture of the two compounds likewise melted at 208.5°. They are, therefore, identical.

Summary

1. Benzalpinacoline, reduced by catalytic means and by metal combinations, yielded 3 new substances.

2. The structure of 2 of these, ω-benzylpinacoline and 2,2,9,9-tetramethyl-5,6-diphenyl-decandione-3,8, have been established by independent syntheses.

3. The third compound, presumably β-phenylethyl-*tert*-butyl carbinol, is still under investigation.

MIDDLETOWN, CONNECTICUT

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

POLYMERIZATION OF ALLYL CINNAMALACETATE[1]

BY F. F. BLICKE

Received April 4, 1923

Acrylic acid, because of its unsaturated nature, is very readily polymerized; the same behavior characterizes the substituted acrylic acids of the type R—CH=CH—COOH.

β-Phenylacrylic acid (cinnamic acid) occurs naturally in several polymeric forms, and in the form of its allyl ester polymerizes under the influence of heat;[2] the ethyl and propyl esters do not polymerize under the same conditions.

Some years ago it was shown that another analog of acrylic acid, β-furfuracrylic acid, when converted into its allyl ester, is also prone to polymerization.[3]

At the suggestion of C. Liebermann, made shortly before his death, a

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[1] This investigation was begun at the Technische Hochschule, Berlin, in 1914, and completed at the University of Michigan.

[2] (a) Liebermann and Zsuffa, *Ber.*, **44**, 841 (1911). (b) Liebermann and Kardos, *ibid.*, **46**, 1055 (1913). Seeligmann, *Dissertation*, Karlsruhe, **1906**.

[3] Blicke, *Ber.*, **47**, 1352 (1913).