[A CONTRIBUTION FROM THE HALL LABORATORY OF CHEMISTRY, WESLEYAN UNIVERSITY]

A REDUCTION PRODUCT OF BENZALPINACOLONE

BY G. ALBERT HILL AND SAMUEL SUSSELMAN

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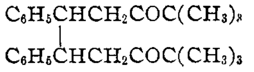
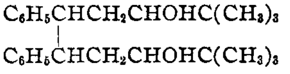
In an earlier paper[1] a compound melting at 142° was mentioned. Because of an error in the determination of the molecular weight, which led to the belief that this substance was a monomolecular reduction product, it was tentatively suggested that this might be β-phenylethyl-*tert.*-butylcarbinol. Subsequently[2] this alcohol was synthesized and it was found to be a liquid, and otherwise different from the substance produced earlier. Consequently, this investigation was undertaken to determine the nature of the solid reduction product.

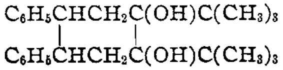
To prepare it in satisfactory yields, benzalpinacolone was reduced by aluminum amalgam. Simultaneously, a known diketone,[1] melting at 208°, was produced in quantity and complicated the isolation of the desired substance. This was purified by a somewhat elaborate process, and then melted at 147°.

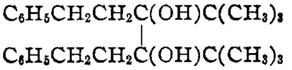
Because there was a possibility that this was mixed-crystal material, some of the solid was successively recrystallized from three different solvents. No separation occurred; all the samples, singly and when mixed, melted at 147°. The cooling curve of the molten material was, in shape, that characteristic of simple compounds, and had a single flat section. These experiments proved this reduction product to be homogeneous, and a compound.

Analytical values, obtained not without difficulty by combustions, indicated that the empirical formula was that of benzalpinacolone. Due to the low solubility of the compound, molecular weight determinations were attempted by an ebullioscopic method only and showed this substance to be a dimolecular reduction product. Since the analyses were complicated by the clusters of methyl groups, the empirical formula calculations are not flawless, and hence it is necessary to consider all of the following as structural possibilities for the compound melting at 147°.

I

$$\begin{array}{l} C_6H_5CHCH_2COC(CH_3)_3 \\ \qquad\;\; | \\ C_6H_5CHCH_2COC(CH_3)_3 \end{array}$$

II

$$\begin{array}{l} C_6H_5CHCH_2CHOHC(CH_3)_3 \\ \qquad\;\; | \\ C_6H_5CHCH_2CHOHC(CH_3)_3 \end{array}$$

III

$$\begin{array}{l} C_6H_5CHCH_2C(OH)C(CH_3)_3 \\ \qquad\;\; | \qquad\quad\; | \\ C_6H_5CHCH_2C(OH)C(CH_3)_3 \end{array}$$

IV

$$\begin{array}{l} C_6H_5CH_2CH_2C(OH)C(CH_3)_3 \\ \qquad\qquad\quad\;\; | \\ C_6H_5CH_2CH_2C(OH)C(CH_3)_3 \end{array}$$

The substance under examination gave no test for hydroxyl with the common reagents, but because of possible steric hindrance, formulas II, III and IV cannot be excluded definitely on this account. A compound

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[1] Hill, Spear and Lachowicz, THIS JOURNAL, **45**, 1557 (1923).

[2] Hill and Bruce, *ibid.*, **52**, 347 (1930).

with structure IV might result from the reduction of benzylpinacolone. When this substance was treated with aluminum amalgam nothing melting at 147° resulted. Compounds II and III might result from the action of reducing agents on I, which is the structure already established synthetically for the benzalpinacolone reduction product melting at 208°. Consequently this diketone was subjected to the action of aluminum amalgam, but without effect.

There remains the possibility that both the solid melting at 147° and that melting at 208°, have a structure represented by I, and hence are stereochemically related. There are two similar asymmetric carbon atoms in I and a meso and a racemic form are therefore possible. On this basis the 147° compound is a diketone. It does not, however, yield an oxime or a phenylhydrazone, although this is not surprising because of the probable steric influence of the tertiary butyl radicals. Furthermore, the 208° compound behaves similarly. The proposed diketone structure was confirmed by the action of methylmagnesium iodide, which added to the compound under investigation in a ratio of 2:1.

Attempts to convert one of the diketonic substances into the other by potassium hydroxide, a forlorn hope at best, were fruitless. No endeavor has been made to specifically designate either of these reduction products as the meso or as the racemic modification.

It is a pleasure to acknowledge the assistance of the Atwater Fund in procuring materials for this study, and also to express our gratitude to Professor E. P. Kohler, through whose kindness the quantitative test with methylmagnesium iodide was made possible.

Experimental

Reduction of Benzalpinacolone.[8]—Ffity grams of benzalpinacolone, 300 cc. of ether, and 20 g. of aluminum amalgam were placed in a one-liter three-necked Woulff flask, equipped with a condenser, and a mechanical stirrer, since stirring increased the yield of desired compound by over one-half. Two cc. of water initiated the reaction. During a twenty-four-hour period 10 cc. of water, in 2-cc. portions, was added. The diketone melting at 208° and the aluminum hydroxide which formed were filtered off, as these solids interfered with good contact of the solution and the reducing agent. The reduction of the filtrate was continued for another twenty-four hours, 20 g. of amalgam and 10 cc. of water being added as before. The reaction mixture and all the products were united and treated with an excess of hydrochloric acid, which dissolved the hydroxide and formed a two-phase liquid system. The ether contained most of the 208° compound in suspension, and, after separation of the layers, this was removed by filtration. The filtrate, and washings, were subjected to distillation at 7 mm. and material collected up to 180°. This fraction had the odor of benzalpinacolone, and is probably composed of the unsaturated ketone and its liquid reduction products. The residue, which crystallized, was treated with 300 cc. of water and ether was added until most of the solid dissolved. The insoluble part melted at 208°. When the ether was

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[8] Hill and Bramann, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1925, Vol. V, p. 15.

concentrated a solid melting at 144–149° resulted. If the fraction melted at 148° or above it was again given the water–ether treatment. If it melted below 147°, it was fractionally crystallized from ether. When pure the reduction product was white and melted at 147°. This material shows an unusual tendency to cling to glass and to porcelain when once deposited, necessitating for its removal washing with warm ether. Forty-eight per cent. of the benzalpinacolone was converted into the diketone melting at 208°, 22% into the 147° compound, and 30% was unaffected, or changed into liquid reduction products.

Tests for Homogeneity

Crystallization Experiments.—Some of the material melting at 147° was successively recrystallized from ethyl alcohol, from ether and from benzene. All fractions melted at 147°. The identity of all the samples was established by mixed melting point determinations.

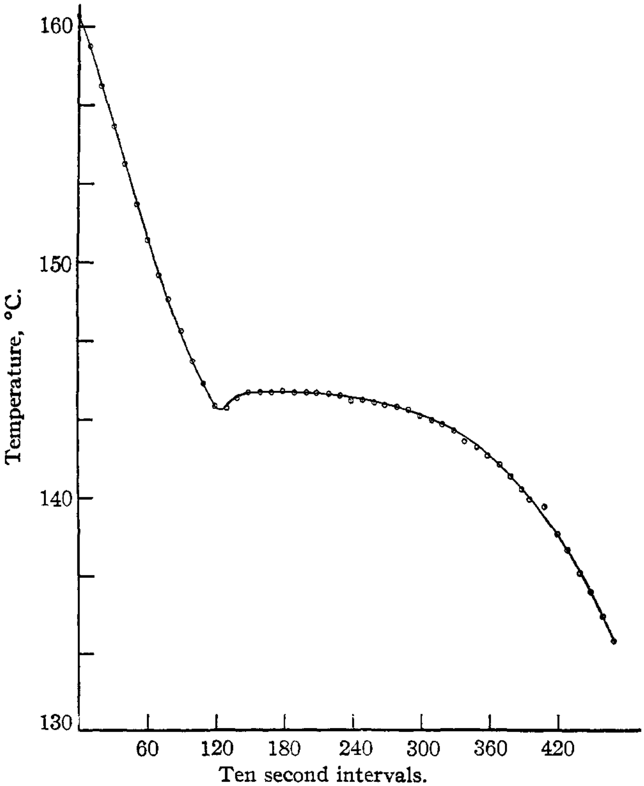

Fig. 1.

Cooling Curves.—About 10 g. of the purified substance was melted in a large Pyrex test-tube. This was then provided with a Beckmann thermometer and a silver stirrer with a glass handle, and placed in a jacket filled with cotton. The molten mass was stirred continuously and thermometer readings were taken every ten seconds. The curve presented here, Fig. 1, is typical of those obtained in three quite independent runs. In all of these the flat section occurred somewhat below the melting point as observed with a short Anschütz thermometer.

Analyses.—The best and most consistent analyses were obtained by burning the compound intimately mixed with cupric oxide powder. In all other cases lower values for carbon resulted.

Sample, g.	CO_2, g.	H_2O, g.	C, %	H, %
0.2006	0.6044	0.1608	82.17	8.97
.2412	.7259	.1903	82.08	9.12
.2033	.6135	.1642	82.30	9.04

The calculated empirical formula is $C_{13}H_{16}O$.

Molecular Weight Determinations.—Menzies' method was used, and to provide adequate checks and to discover association or dissociation, if possible, two quite different solvents, benzene and carbon tetrachloride, were employed: b. p. benzene, 79.80°; volume of benzene at the boiling point, 30.8 cc.; conversion factor, 0.005003° per mm. B. p. carbon tetrachloride, 76.50°; volume of carbon tetrachloride at the boiling point, 29.1 cc.; conversion factor, 0.005618° per mm.

Solvents	Depression	Sample, g.	Molecular weight
C_6H_6	2.35	0.376	331
C_6H_6	3.30	.547	343
C_6H_6	5.30	.914	359
CCl_4	2.45	.405	332
CCl_4	3.42	.574	333
CCl_4	5.51	.931	334.5

The average of these determinations is 339. Twice the empirical formula weight is 376.

Tests for Functional Groups.—Tests for unsaturation with a carbon tetrachloride solution of bromine, for hydroxyl by the Schotten–Baumann method, and for carbonyl with phenylhydrazine and with hydroxylamine were negative.

Reduction Experiments.—Thirty grams of benzylpinacolone treated with aluminum amalgam in moist ether for three days yielded 25 g. of a liquid mixture boiling at 110–145° at 2 mm. No substance melting at 147° was found.

Forty grams of the 208° diketone was subjected to reduction, as above, for six days. The prolonged action was deemed wise because of the very slight solubility of this substance; 37 g. of the compound was recovered.

Test with a Grignard Reagent.[4]—With methylmagnesium iodide, the amount of methane evolved was found to be 0.32 mole, while 2.04 moles of the Grignard reagent was used per molecule of the substance being investigated.

Treatment of the Diketones with Alkali.—Three grams of the 147° diketone was refluxed for twenty hours, in 150 cc. of ethyl alcohol containing 40 g. of potassium hydroxide. When added to water the reaction mixture gave a precipitate. This was washed and recrystallized from ether. It weighed 2.5 g. and melted at 147°.

When 3 g. of the diketone melting at 208° was similarly treated 2.4 g. was recovered unchanged.

Summary

The benzalpinacolone reduction product reported as melting at 142°, and once tentatively regarded as β-phenylethyl-*tert.*-butylcarbinol, has been found to melt when pure at 147°. It has been shown to be a stereo-

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[4] This experiment was carried out in the Converse Laboratory of Harvard University.

isomer of the 2,2,9,9-tetramethyl-5,6-diphenyl-decandione-3,8, melting at 208°.

Middletown, Connecticut

[Contribution from the Chemical Laboratory, Stanford University]

SALTS OF THE TOLYL AND MIXED PHENYL-TOLYL SELENONIUM HYDROXIDES[1]

By H. M. Leicester and F. W. Bergstrom

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Introduction

In a previous investigation,[2] which had for its original purpose a study of trialkyl and triaryl selenonium radicals and their approximate placement in an electropotential series, a number of salts of triphenylselenonium hydroxide were prepared. The primary material from which all of these salts were obtained was triphenylselenonium chloride, the product of the action of diphenyl selenium dichloride upon benzene in the presence of aluminum chloride. The following equations indicate the steps in this synthesis:

$$2C_6H_5N_2Cl + K_2Se_x = (C_6H_5)_2Se + 2KCl + 2N_2 + (x - 1)Se \qquad (1)$$

$$(C_6H_5)_2Se + O \xrightarrow{HNO_3} (C_6H_5)_2SeO \qquad (2)$$

$$(C_6H_5)_2SeO + 2HCl = (C_6H_5)_2SeCl_2 + H_2O \qquad (3)$$

$$(C_6H_5)_2SeCl_2 + C_6H_6 \xrightarrow{AlCl_3} (C_6H_5)_3SeCl + HCl \qquad (4)$$

In continuation of this work, we have prepared salts of *m*- and *p*-tolyl and of mixed phenyl-*p*-tolyl selenonium hydroxides and have developed a method of synthesis that may throw some light upon the relative electronegativities of the aryl groups attached to the selenium.

Preparation of Triarylselenonium Salts.—Since the synthesis of triphenyl selenonium chloride described in our earlier paper was so readily effected by condensing diphenyl selenium dichloride with benzene in the presence of aluminum chloride, in accordance with equations 1–4 above, it was correctly surmised that the tri-*p*-tolyl and many of the mixed phenyl-tolyl selenonium salts could be prepared in the same manner. Thus, symmetrical diarylselenium dichlorides were made from potassium polyselenide and the appropriate diazotized amine (aniline, *m*- or *p*-toluidine) as represented by equation 1.[3] Di-*m*- and di-*p*-tolyl selenides were prepared in this manner and converted by the action of concentrated nitric

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[1] From the Ph.D. dissertation of Dr. Leicester. A paper presented at the Eugene, Oregon, meeting of the A. A. A. S., June, 1930 and at the Cincinnati meeting of the American Chemical Society, September, 1930.

[2] Leicester and Bergstrom, This Journal, 51, 3587 (1929).

[3] This method was first described by Schoeller, *Ber.*, 52, 1517 (1919), and somewhat extended in our earlier paper.