presence of the latter was attributed to water in the reagents which had presumably hydrolyzed the tribromo ethyl ester first formed in the reaction. The experiment was, therefore, repeated with carefully dried chloroform and bromine which had been distilled from phosphorus pentoxide. The product melted with decomposition over a long range, showing it to be probably a bromo addition compound but very impure. Repeated trials have not as yet given a pure substance. When this crude product was treated with water, a copious yield of the aldehyde was obtained.

When ethyl 2,4-dimethoxycinnamate (68–69°), prepared by the Claisen condensation, was distilled under diminished pressure, a yellow oil boiling at 219° (22 mm.) was obtained. This distillate solidified on cooling and, on crystallization from low boiling petroleum ether, separated in perfectly colorless needles melting at 61°. A mixture of this ester and the one previously used (68–69°) melted from 45–55°. Analysis proved it to be an isomeric form.

Anal. Subs., 0.1148: CO_2, 0.2777; H_2O, 0.0730. Calcd. for $C_{13}H_{16}O_4$: C, 66.10; H, 6.78. Found: C, 65.97; H, 7.05.

This isomeric ester on bromination with the usual laboratory reagents or with those that had been carefully dried gave, in quantitative yield, the ethyl ester of 2,4-dimethoxy-5-bromocinnamic acid dibromide (VI) previously described.

Summary

The bromination of 2,4-dimethoxycinnamic acid and its methyl and ethyl esters has been described. The acid differs from *p*-methoxycinnamic acid and from *o*-methoxycinnamic acid in the fact that addition of bromine is invariably accompanied by bromination in the ring and in the extraordinary ease of replacement of the β-bromine atom in the bromination products by alkoxyl groups. The two isomeric ethyl esters of the acid give different products on bromination.

NEW YORK, N. Y.

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

BENZYLPINACOLONES AND THEIR REDUCTION PRODUCTS. I

BY G. ALBERT HILL AND WILLIAM F. BRUCE

RECEIVED JULY 29, 1929 PUBLISHED JANUARY 8, 1930

Sodamide syntheses,[1] in ether, with pinacolone and benzyl chloride yielded mono- and dibenzylpinacolones, $C_6H_5CH_2CH_2COC(CH_3)_3$, $(C_6H_5CH_2)_2CHCOC(CH_3)_3$. Benzylpinacolone has been described by one of us[2] but an improved method of preparation is reported here.

Dibenzylpinacolone in toluene reacted with sodamide and benzyl chloride producing tribenzylpinacolone, $(C_6H_5CH_2)_3CCOC(CH_3)_3$. Good yields resulted in this synthesis only when the original ketone, a readily purified crystalline solid, was distilled just prior to the runs. Possibly this is due to a higher proportion of an enolic modification in the freshly distilled material.

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

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

Only the monobenzylpinacolone gave a crystalline oxime. Probably because of steric hindrance the more highly substituted ketones failed to react. All the ketones were reduced to the corresponding secondary alcohols by the action of sodium and absolute ethyl alcohol. Among the methods employed, which proved unattractive, were the use of sodium and amyl alcohol, sodium and moist ether, magnesium activated by mercuric chloride and absolute methyl alcohol, aluminum and solid potassium hydroxide in absolute ethyl alcohol and zinc and acetic acid.

Of the alcohols, only the tribenzyl derivative failed to give a crystalline phenylurethan.

The β-phenylethyl-*tert.*-butylcarbinol, $C_6H_5CH_2CH_2CHOHC(CH_3)_3$, is a liquid at room temperature. This is interesting because in the course of an earlier investigation of benzalpinacolone,[3] a compound was obtained which was thought to be this, then unknown, carbinol, but which melted at 142°. With the idea of reconciling these two reports, work on the substance melting at 142° has been resumed.

Attempts to reduce the ketones to the corresponding hydrocarbons by a wide variety of methods were unsuccessful save in the case of the monobenzyl compound. Heating with hydriodic acid and red phosphorus under pressure did, however, bring about reduction in this case. The Clemmensen method,[4] of which much was expected, gave only negative results.

Experiments with these ketones and alcohols, which it is hoped will yield the desired hydrocarbons, are being continued in this Laboratory.

It is a pleasure to acknowledge here the assistance in the preliminary work afforded by J. S. Lachowicz and E. W. Flosdorf, and gratefully to mention the material aid from the Atwater Fund.

Experimental Part

Pinacol Hydrate.—This was made according to Adams and Adams.[5]

Pinacolone.—The preparation was according to Hill and Flosdorf.[6]

The Ketones.—Mono-, di- and tribenzylpinacolones were prepared by methods essentially similar; therefore, the detailed procedure for the monobenzyl derivative only is given.

Monobenzylpinacolone.—A modification of the method of Hill and Lachowicz[3] was employed: 41 g. of finely ground friable sodamide was placed in a 2-liter, 3-necked flask provided with a reflux condenser, a mechanical stirrer with a mercury seal and a separatory funnel. A solution of 100 g. of pinacolone in 450 cc. of absolute ether was *slowly* introduced. The loss of ether and pinacolone swept out of the flask by the vigorous evolution of ammonia during the first half hour warranted the use of a trap bottle, im-

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[3] Ref. 2, p. 1561.

[4] Clemmensen, *Ber.*, **46**, 1841 (1913).

[5] R. Adams and E. W. Adams, "Organic Syntheses," John Wiley and Sons, Inc., New York, Vol. V, 1925, p. 87.

[6] G. A. Hill and E. W. Flosdorf, *ibid.*, p. 91.

mersed in a freezing mixture, beyond the reflux condenser to collect the valuable pinacolone. The ether solution was boiled for from eight to ten hours, when evolution of ammonia had practically ceased; 132 g. of pure benzyl chloride was added very slowly, two or three drops a second, to avoid generation of too much ether vapor. The mixture was then warmed and stirred for twenty-four hours; 250 cc. of water was added and the ether layer removed. The latter was washed with water, dilute hydrochloric acid, and again with water, and dried with calcium chloride. After elimination of the ether, the residue was vacuum distilled: 106 g. of monobenzylpinacolone, a 56% yield, was obtained, accompanied by 60 g. of dibenzylpinacolone. These products account for 77.5% of the pinacolone used.

Monobenzylpinacolone is colorless when pure, and while insoluble in water dissolves readily in organic solvents; b. p. (10 mm.) 132°; (43 mm.) 155°; (760 mm.) 247°; d^{20}_{20} 0.95005; d^{20}_{4} 0.9483. The refractive index, n^{20}_{D}, is 1.4999. The dispersion factor found, $N_F - N_C$, is 0.01440. The molecular refraction, calculated by the Lorentz and Lorenz formula, is 58.8 while the values of Eisenlohr[7] give 58.6.

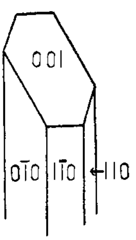
The oxime, prepared by Tanny's method,[8] melted at 95.5°, in agreement with the reported figure.

Dibenzylpinacolone.—The crude product was distilled, b. p. (9 mm.) 190–220°. The viscous yellow distillate solidified and after two crystallizations from ethyl alcohol melted at 49°. The yield of white crystalline material was 59%.

When pinacolone was treated with somewhat more than double the theoretical amount of sodamide and of benzyl chloride required for monosubstitution, a 66.6% yield of dibenzylpinacolone could be obtained without first isolating monobenzylpinacolone. An attempt to prepare an *oxime* was unsuccessful.

Anal. Subs., 0.1814, 0.1509: CO_2, 0.5691, 0.4743; H_2O, 0.1399, 0.1173. Calcd. for $C_{20}H_{24}O$: C, 85.66, H, 8.63. Found: C, 85.56, 85.69; H, 8.63, 8.70.

Crystal Structure of Dibenzylpinacolone.[9]—Triclinic system; prismatic habit. Positive unit prism 110; negative unit prism $1\bar{1}0$; side pinacoid $0\bar{1}0$. $110 > 1\bar{1}0$ = 140° 33′; $1\bar{1}0 > 010$ = 97° 33′; $110 > 0\bar{1}0$ = 121° 52′. Parameters: $a = 0.35735$; $b = 1.00000$; $c = 0.00000$. No good faces near 001 were obtained, but a conchoidal cleavage parallel to 001 was found.



Tribenzylpinacolone.—The apparatus used was similar to that previously described save that the stirrer passed through a close-fitting glass bearing tube, which extended into the solution, instead of through a mercury seal bearing. It was observed that when small amounts of mercury were prevented from passing into the reactants, the yields were better. Toluene was used as a solvent instead of ether. Pure tribenzylpinacolone was prepared by recrystallization from toluene, m. p. 161.5° (corr.). Yields as high as 73.4% were obtained.

Anal. Subs., 0.1983, 0.2372: CO_2, 0.6345, 0.7598; H_2O, 0.1442, 0.1721. Calcd. for $C_{27}H_{30}O$: C, 87.51; H, 8.17. Found: C, 87.26, 87.35; H, 8.14, 8.12.

The boiling point is (8 mm.) 268.9° (corr.). The calculated molecular weight is 370.2; found by Menzies' method, using benzene, 363.6, 365.2.[10]

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[7] Eisenlohr, *Z. physik. Chem.*, **75**, 585 (1911).

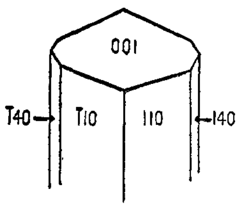
[8] Tanny, *Ber.*, **15**, 2781 (1882).

[9] Studies of the crystal structures were made with the assistance of Professor W. G. Foye.

[10] Determination by B. C. French.

This ketone dissolves in toluene, quite readily when hot, but is only soluble to the extent of somewhat over 1 g. in 100 cc. of boiling alcohol. Boiling ether dissolves twice as much. It dissolves easily in hot carbon tetrachloride. An attempt to prepare an *oxime* was not successful.

Crystal Structure of Tribenzylpinacolone.—Orthorhombic system; columnar habit. Base 001; unit prism 110; brachyprism 140. 140 > $\bar{1}40$ = 131° 08′; 110 > $1\bar{1}0$ = 132° 45′; 110>140 = 138° 22′. Parameters: a = 0.043741; b = 1.00000; c = 0.00000. Fair basal cleavage, very good prism cleavage.



The Secondary Alcohols.—The most successful method employed for the reduction of the ketones to the corresponding secondary alcohols was ultimately used with all three, and hence the preparation of but one will be given in detail.

β-Phenylethyl-*tert.*-butylcarbinol.—Thirty-eight grams of monobenzylpinacolone dissolved in 280 cc. of absolute ethyl alcohol was treated, with stirring and refluxing, with 51 g. of sodium. This required about twenty minutes and stirring was continued for three hours; 200 cc. of water was added, and the resulting two-layer system separated. The aqueous part was made acid with hydrochloric acid and a small amount of oily material separated. This was added to the non-aqueous layer, which was washed with water, dilute hydrochloric acid and water, and after the addition of a little ether, about 50 cc., dried with sodium sulfate. By vacuum fractionation at 15.5 mm., the corrected boiling point was found to be 145.5°, and 28.5 g. of the carbinol, a yield of 73%, was procured.

Anal. Subs., 0.47680, 0.17990,[11] 0.26575; CO_2, 1.4144, 0.53380, 0.78810; H_2O, 0.44310, 0.16720, 0.24720. Calcd. for $C_{13}H_{20}O$: C, 81.18; H, 10.42. Found: C, 80.90, 80.93, 80.88; H, 10.40, 10.40, 10.40.

The carbinol is a colorless oily liquid insoluble in water and readily soluble in organic solvents; d_{20}^{20} 0.9593; d_4^{20} 0.9578; n_D^{20} 1.5097; $N_F - N_C$, 0.01456; M_D, calculated from the refractive index, 60.16; calculated from the Eisenlohr values, 60.158.

Preparation of the Phenylurethan.—Ten grams of the carbinol was mixed with 6.5 g. of phenylisocyanate and set aside, in a closed flask, for two days; 20 cc. of ethyl alcohol was then added and the flask warmed to bring about complete solution. On cooling the filtered material, microscopic white crystals separated, m. p. 88.1° (corr.).

Anal. (Kjeldahl). Subs., 0.5788, 0.5403: acid used, 20.56 cc. of 0.09232 N, 20.08 cc. of 0.08351 N H_2SO_4. Calcd. for $C_{20}H_{25}O_2N$: N, 4.50. Found: N, 4.58, 4.33.

(Dibenzylmethyl)-*tert.*-butylcarbinol.—This carbinol, b. p. (15 mm.) 206–208°, was obtained in a 32% yield.

Anal. Subs., 0.1998, 0.2068: CO_2, 0.6219, 0.6438; H_2O, 0.1636, 0.1694. Calcd. for $C_{20}H_{26}O$: C, 85.05; H, 9.28. Found: C, 84.90, 84.88; H, 9.17, 9.16.

This alcohol is colorless when pure, and is extremely viscous. While it could be solidified, apparently, at low temperatures, it was not obtainable crystalline despite numerous and various attempts; d_{20}^{20} 1.005; n^{20}, using daylight, 1.5422, 1.5440; $N_F - N_C$, 0.01755. The phenylurethan was deposited as fine, white needles, m. p. 148°.

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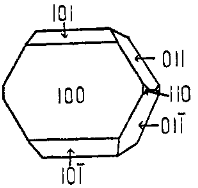
[11] Analysis by E. T. Dowling.

Anal. (Kjeldahl). Subs., 0.7512:[12] acid used, 18.34 cc. of 0.10372 *N* H_2SO_4. Calcd. for $C_{27}H_{31}O_2N$: N, 3.49. Found: N, 3.54.

(Tribenzylmethyl)-*tert.*-butylcarbinol.—Some of this carbinol was prepared by the action of sodium and amyl alcohol on the ketone, but the method was no better than the foregoing, which, in the presence of a little toluene, gave a yield of 45%, m. p. 156.5° (corr.). An attempt to form a phenylurethan was unsuccessful.

Anal. Subs., 0.2418, 0.2868: CO_2, 0.7723, 0.9137; H_2O, 0.1869, 0.2203. Calcd. for $C_{27}H_{32}O$: C, 87.03; H, 8.67. Found: C, 86.94, 86.88; H, 8.65, 8.60.

Crystal Structure of (Tribenzylmethyl)-*tert.*-butylcarbinol.—Orthorhombic system; tabular habit. Front pinacoid 100; brachydome 011; macrodome 101; indistinct unit prism 110. 011 > $01\bar{1}$ = 93° 15′; 011 > $0\bar{1}1$ = 86° 45′; 100 > 101 = 135° 33′; 101 > $\bar{1}01$ = 88° 46′. Parameters: a = 0.94482; b = 1.00000; c = 1.0218.



The Hydrocarbons.—Despite numerous and various attempts to reduce the ketones and carbinols to hydrocarbons, only that derived from the monobenzyl compound has been obtained.

2,2-Dimethyl-5-phenyl-pentane.—Nine and one-half grams of monobenzylpinacolone, 1.7 g. of red phosphorus and 25.6 g. of 57% hydriodic acid were heated to 180–190° in a sealed tube for twelve hours. The contents of the cooled tube was placed in 150 cc. of 1:15 sulfuric acid and mossy zinc was added. After one and one-half hours the product was removed by ether, the ether solution was washed with water, dilute sodium hydroxide, and water, and dried with calcium chloride. Upon repeated fractionation, after removal of the ether (4 g.) a 46% yield of hydrocarbon resulted; b. p. (9 mm.) 115°.

Anal. Subs., 0.1701, 0.2218, 0.1592, 0.2030: CO_2, 0.5555, 0.7243, 0.5192, 0.6571; H_2O, 0.1584, 0.2063, 0.1479, 0.1882. Calcd. for $C_{13}H_{20}$: C, 88.55, H, 11.44. Found: C, 89.06, 89.06, 88.94, 88.28; H, 10.41, 10.43, 10.40, 10.40.

The pure substance was colorless and an acetone solution of potassium permanganate was only very slowly reduced when in contact with it. Molecular weight, calcd. for $C_{13}H_{20}$: 176.16; found, by Menzies' method, 189, 178; d_{20}^{20} 0.9460; d_4^{20} 0.9443; n^{20}, using daylight, 1.5281, 1.5267; $N_F - N_C$, 0.01615; M_D, from refractive index, 57.39; from Eisenlohr's values, 58.63.

Summary

1. Mono-, di- and tribenzylpinacolones, a series of highly substituted acetones, and their corresponding secondary alcohols have been prepared.

2. One hydrocarbon, 2,2-dimethyl-5-phenyl-pentane, related to the simplest of the ketones, has been produced.

3. Experiments leading to the other hydrocarbons are in progress.

Middletown, Connecticut

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[12] Analysis by F. H. Adams..