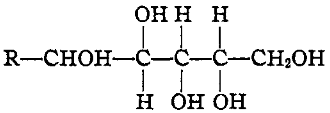
TABLE II

C-SUBSTITUTED PENTITOLS



$$R{-}CHOH{-}\underset{H}{\overset{OH}{C}}{-}\underset{OH}{\overset{H}{C}}{-}\underset{OH}{\overset{H}{C}}{-}CH_2OH$$

						% Composition					
						C		H		OH[7]	
R—	$[\alpha]^{25}$D Pyridine	Concn., g./100 cc.	M. p. (cor.), °C.	Yield, %	Formula	Calcd.	Found	Calcd.	Found	Calcd.	Found
Cyclohexyl	+12.6	4.9	148	90	$C_{11}H_{22}O_5$	56.39	56.49	9.47	9.25	36.3	35.7
Phenyl	−37.7	1.0	137	90	$C_{11}H_{16}O_5$	57.88	57.95	7.09	7.07	..	..
Naphthyl	−70.2	3.6	187	5	$C_{15}H_{18}O_5$	64.75	64.70	6.87	6.50	30.6	30.3

C-Substituted Pentitols.—The above 1-C-substituted di-isopropylidene-pentitols were hydrolyzed by refluxing with about 15 volumes of 10% acetic acid for four hours. The clear solutions were evaporated to dryness and the products recrystallized from 95% ethanol to constant rotation and melting point.

The low yield in the case of the 1-C-naphthyl-pentitol is due to the repeated recrystallizations required to separate the mixture of stereoisomers. By a hydrolysis of crude 1-C-phenyl-di-isopropylidine-pentitol and subsequent fractional crystallization from butanol a very small yield of a dextro-rotatory isomer of m. p. 167° was obtained. The amount of material, however, was insufficient to permit purification to constant rotation in this case. This compound was analyzed: *Anal.* Calcd. for $C_{11}H_{16}O_5$: C, 57.88; H, 7.09. Found: C, 57.68; H, 7.25. Since the objective of this work did not require the isolation of both isomers in a pure state at this time, no further efforts were made to characterize the more soluble forms. The properties of the less soluble forms are given in Table II.

1-C-Cyclohexyl-1,2,3,4-tetraacetyl-5-trityl-pentitol.—1-C-cyclohexylpentitol (6.2 g.) was treated at room temperature in dry pyridine solution with one equivalent of triphenylmethyl chloride and allowed to stand overnight. At the end of this time 31 cc. of acetic anhydride was added at ice temperature and the mixture allowed to stand two days. When the reaction mixture was added to ice water, dropwise, the 1-C-cyclohexyl-1,2,3,4-tetraacetyl-5-trityl-pentitol precipitated and could then be crystallized from ethanol. The yield of product of m. p. 134°, $[\alpha]^{25}$D −15.0°, pyridine 5.3 g. in 100 cc., was 17.1 g. (90%).

Anal. Calcd. for $C_{38}H_{44}O_9$: C, 70.79; H, 6.88. Found: C, 70.68; H, 6.84.

Summary

Three new crystalline C-substituted pentitols have been prepared from di-isopropylidene-aldehydo-L-arabinose.

NEW HAVEN, CONN. RECEIVED AUGUST 29, 1945

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[7] Peterson, Hedberg and Christensen, *Ind. Eng. Chem., Anal. Ed.*, **15**, 225 (1943).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Attempts to Prepare Cyclopolybenzoylenes[1]

BY C. F. KOELSCH AND C. E. BRYAN

If a *p*-phenylene group is a rigid structure with bonds at an angle of 180°, and if attachment of two such groups to a carbon atom does not change the normal carbon valence angle, it should be possible to obtain cyclopoly-*p*-benzoylenes (I) when $n = 5$ or 6, from the corresponding dibasic acids (II). Experiments with this end in view have now been carried out, but with negative results.

$(COC_6H_4)_n$

I

$HO(COC_6H_4)_nCOOH$

II

Previous data have indicated that the valences joining the phenyl groups with the carbonyl carbon in benzophenone are inclined at an angle of 131–134°[2] (or 122–128°[3]). However, in the present work, no indication was had of the formation of cyclooctabenzoylene[4] when the calcium salt of II, $n = 4$ was pyrolyzed.

Failure to obtain cyclopolybenzoylenes may be a result of either or both of two conditions, each of which tends to be caused by resonance interaction of the linking carbonyl groups with the benzene rings. (1) The acids (II) through resonance alone have more linear structures than would be supposed from previous data[5]; and (2) the benzene rings are co-planar with each other and with the plane containing the bonds linking them to the carbonyl carbon, interference of *o*-hydrogen atoms thus tending to keep the chain nearly linear and rigid.

Experimental[6]

***p*$_2$-Terbenzone-*p*$_1$,*p*$_3$-dicarboxylic Acid** (II, $n = 3$).[7]—Terephthalic acid (100 g.) and phosphorus pentachloride

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[1] From the Ph. D. Thesis of Carl Eddington Bryan, August, 1942.

[2] Sutton and Hampson, *Trans. Faraday Soc.*, **31**, 945 (1935); Bergmann, Engel, and Mager, *Ber.*, **65**, 446 (1932).

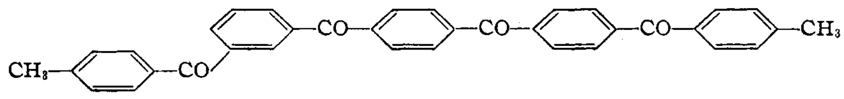
[3] Coomber and Partington, *J. Chem. Soc.*, 1445 (1938).

[4] The angle at the vertex of a regular octagon is 135°.

[5] *Cf.* Lüttringhaus and Buchholz, *Ber.*, **73**, 137 (1940).

[6] Temperatures reported are uncorrected. Those above 300° were measured using a 510° thermometer which showed the b. p. (748 mm.) of mercury to be 358° (literature 356°) and that of sulfur to be 441° (literature 443°).

[7] Application of existing systems of nomenclature to some of the substances prepared leads to awkward names, not conducive to easy visualization. It appeared worthwhile, therefore, in such cases to use a new system for "polybenzones" analogous to the one now used for polyphenyls. *p*-Dibenzoylbenzene thus may be called *p*$_2$-terbenzone, *p*$_2$ indicating *para* substitution in the second ring; *p*,*p*′-dibenzoylbenzophenone-*p*″,*p*‴-dicarboxylic acid receives the name *p*$_2$,*p*$_3$-quaterbenzone-*p*$_1$,*p*$_4$-dicarboxylic acid; the compound



would be named *p*$_1$,*p*$_5$-dimethyl-*m*$_2$,*p*$_3$,*p*$_4$-quinquebenzone.

(253 g.) gave terephthalyl chloride, b. p. 135-150° at 10 mm., m. p. 79-80°, in a yield of 117 g. (96%). This with 900 ml. of toluene and 165 g. of aluminum chloride gave p_1,p_3-dimethyl-p_2-terbenzone (131 g., 73%), m. p. 188-189° (reported, m. p. 188°,[8] 194°[9]).

Anal. Calcd. for $C_{22}H_{18}O_2$: C, 84.1; H, 5.7. Found: C, 83.9; H, 5.7.

A solution of 10 g. of p_1,p_3-dimethyl-p_2-terbenzone and 3.7 ml. of bromine in 75 ml. of acetic acid was boiled over a 200-watt light bulb for four hours. The mixture was then cooled, and the solid (10.2 g., m. p. 184-190°) was removed and crystallized several times from acetic acid giving 2.5 g. (17%) of **p_1,p_3-di-(bromomethyl)-p_2-terbenzone,** colorless plates, m. p. 204-206°.

Anal. Calcd. for $C_{22}H_{16}Br_2O_2$: C, 55.9; H, 3.4; Br, 33.9. Found: C, 56.2; H, 3.5; Br, 34.3.

When 0.76 g. of the dibromo compound was boiled for two hours with 15 ml. of acetic acid containing 0.9 g. of potassium acetate, it gave 0.69 g. (96%) of **p_1,p_3-di-(acetoxymethyl)-p_2-terbenzone,** colorless plates from acetic acid, m. p. 171-172°.

Anal. Calcd. for $C_{26}H_{22}O_6$: C, 72.6; H, 5.1. Found: C, 72.3; H, 5.3.

The diacetate (0.25 g.) boiled for twenty minutes with 100 ml. of 10% sodium hydroxide in methanol, gave 0.17 g. (85%) of **p_1,p_3-di-(hydroxymethyl)-p_2-terbenzone,** colorless plates from ethyl acetate, m. p. 230-231°.

Anal. Calcd. for $C_{22}H_{18}O_4$: C, 76.3; H, 5.2. Found: C, 76.4; H, 5.3.

A solution of 1.6 g. of the dihydroxy compound and 1.4 g. of chromic anhydride in 90 ml. of acetic acid, boiled and stirred for eight hours, gave 1.67 g. (97%) of **p_2-terbenzone-p_1,p_3-dicarboxylic acid,** which sintered at 390° and melted at 395-398° (reported,[9] m. p. 390.5°, decomp. 395°).

The same acid was obtained more simply, directly from p_1,p_3-dimethyl-p_2-terbenzone. A mixture of 20 g. of the diketone, 50 g. of chromic anhydride and 500 ml. of acetic acid was heated under reflux and stirred for twenty hours. A second 50-g. portion of chromic anhydride was then added, and stirring and boiling were continued for twenty-four hours. The solid product was removed, washed with acetic acid, warm 10% sulfuric acid, and water, and dried, giving 22.3 g. (94%) of crude product. The acid crystallized well from pyridine as its **pyridine salt,** a compound which lost all of its pyridine when it was heated at 130°.

Anal. Calcd. for $C_{22}H_{14}O_6 + 2C_5H_5N$: C_5H_5N, 29.6. Found: C_5H_5N, 29.1.

The residual acid melted at 394-398°. Its neutral equivalent (calcd., 187; found, 192) was determined by dissolving a sample (0.4 g.) in excess 0.04 *N* sodium hydroxide, and back titrating to phenolphthalein with standard acid.

A mixture of 0.5 g. of the acid and 0.4 g. of copper chromite[10] in 10 ml. of quinoline was boiled for five hours, giving 0.21 g. (55%) of *p*-dibenzoylbenzene, m. p. 157-159° alone and 158-160° when mixed with an authentic sample.

A suspension of 15 g. of the acid in 500 ml. of thionyl chloride, boiled for four hours and then distilled to dryness, gave **p_2-terbenzone-p_1,p_3-dicarbonyl chloride,** colorless crystals (10.4 g., 63%) from toluene, m. p. 210-213°.

Anal. Calcd. for $C_{22}H_{12}Cl_2O_4$: C, 64.2; H, 2.9. Found: C, 64.5; H, 2.9.

When the acid chloride was boiled with alcohol for two hours it was converted quantitatively into **ethyl p_2-terbenzone-p_1,p_3-dicarboxylate,** colorless plates from ethyl acetate, m. p. 196-197°. The same ester was obtained in a yield of 61% by boiling the acid for three days with 7% alcoholic sulfuric acid.

Anal. Calcd. for $C_{26}H_{22}O_6$: C, 72.6; H, 5.1. Found: C, 72.6; H, 4.9.

No pure substance (*desoxycyclopentabenzoylene*) could be obtained from the mixture resulting when p_2-terbenzone-p_1,p_3-dicarbonyl chloride reacted with diphenylmethane and aluminum chloride in nitrobenzene. Moreover, when calcium p_2-terbenzone-p_1,p_3-dicarboxylate (obtained as an insoluble precipitate from the sodium salt and calcium chloride in water) was pyrolyzed, it gave a dark red liquid containing a very small amount of yellow solid, and no pure substance (*cyclohexabenzoylene*) could be isolated from this.

p_2,p_1-Quaterbenzone-p_1,p_4-dicarboxylic Acid (II, n = 4).—A mixture of 21 g. of *p,p'*-dimethylbenzophenone,[11] 40 g. of chromic anhydride, and 250 ml. of acetic acid was boiled and stirred for five hours, then an additional 30 g. of chromic anhydride was added, and heating and stirring were continued for five hours. The resulting benzophenone-*p,p'*-dicarboxylic acid (21.8 g., 81%), m. p. 360-365° in a sealed tube (reported[8] m. p. above 360°), was heated under reflux for four hours with 500 ml. of thionyl chloride. This gave benzophenone-*p,p'*-dicarbonyl chloride, faintly yellow crystals from ligroin (19 g., 78%), m. p. 132-133° (reported[8] m. p. 133°). The acid chloride, with 300 ml. of toluene and 25 g. of aluminum chloride, gave 19.9 g. (76%) of **p_1,p_4-dimethyl-p_2,p_3-quaterbenzone,** colorless platelets from acetic acid, m. p. 248-250°.

Anal. Calcd. for $C_{29}H_{22}O_3$: C, 83.3; H, 5.3. Found: C, 83.6; H, 5.4.

A mixture of 8 g. of p_1,p_4-dimethyl-p_2,p_3-quaterbenzone, 25 g. of chromic anhydride, 3 ml. of sulfuric acid, and 500 ml. of acetic acid was boiled and stirred for thirty hours, two more portions of chromic anhydride and sulfuric acid (each 25 g. and 3 ml.) being added at ten-hour intervals. The solid product (9.0 g.) was removed, washed well with dilute sulfuric acid, crystallized from pyridine, and then washed with acetic acid and water. There was obtained 7.1 g. (77%) of **p_2,p_3-quaterbenzone-p_1,p_4-dicarboxylic acid,** colorless platelets, m. p. 396-398° with decomposition.

Anal. Calcd. for $C_{29}H_{18}O_7$: C, 72.8; H, 3.8. Found: C, 73.3; H, 3.9.

The neutral equivalent (calcd. 239; found: 243, 244, 241) was determined by diluting a solution of 0.3 g. of the acid in 40 ml. of 0.1 *N* sodium hydroxide to 250 ml. and rapidly back titrating in the cold to an immediate end-point, the sodium salt otherwise undergoing extensive hydrolysis.

Decarboxylation of 0.2 g. of the acid by distilling it from copper chromite at 10 mm. gave 0.1 g. of quaterbenzone, colorless platelets from acetic acid, m. p. 224-225° (reported[12] m. p. 227°). The same compound was obtained in a yield of 74% from benzophenone-*p,p'*-dicarbonyl chloride (1.6 g.), benzene and aluminum chloride.

When 0.25 g. of the acid was boiled for thirty-six hours with 250 ml. of thionyl chloride, it gave **p_2,p_3-quaterbenzone-p_1,p_4-dicarbonyl chloride.** This compound separated from hot xylene as a white gelatinous mass that dried to a nearly colorless powder and it was not obtained pure; m. p. 418-422° with decomposition.

Anal. Calcd. for $C_{29}H_{16}Cl_2O_5$: C, 67.6; H, 3.1. Found: C, 68.6; H, 4.7.

No pure substance (*cycloöctabenzoylene*) was isolated from the red liquid obtained when a mixture of 0.3 g. of p_2,p_3-quaterbenzone-p_1,p_4-dicarboxylic acid and 0.3 g. of calcium oxide was heated for two and one-half hours at 390°.

p_2,p_3,p_4-Quinquebenzone-p_1,p_5-dicarboxylic Acid (II, n = 5).—A warm solution of 5 g. of p_2-terbenzone-p_1,p_3-dicarbonyl chloride in 300 ml. of toluene was treated with 7.3 g. of aluminum chloride, and the mixture was heated on a steam-bath with occasional shaking for two hours. Decomposition with iced hydrochloric acid gave 5.7 g. (90%) of crude product, and repeated crystallization of this from pyridine gave 2.5 g. (40%) of **p_1,p_5-dimethyl-p_2,p_3,p_4-quinquebenzone,** colorless platelets, m. p. 303-304°.

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[8] Limpricht, *Ann.*, **312**, 91 (1900).

[9] Connerade, *Bull. soc. chim. Belg.*, **40**, 144 (1931).

[10] Connor, Folkers and Adkins, This Journal, **54**, 1138 (1932).

[11] Gomberg and Todd, *ibid.*, **39**, 2392 (1917).

[12] Connerade, *Bull. soc. chim. Belg.*, **42**, 311 (1932).

Anal. Calcd. for $C_{36}H_{26}O_4$: C, 82.8; H, 5.0. Found: C, 83.0; H, 5.0.

When 0.9 g. of this substance was boiled and stirred for five hours with 125 ml. of acetic acid containing 14 g. of chromic anhydride and 5 ml. of concd. sulfuric acid, it gave 0.96 g. (96%) of crude dibasic acid, m. p. 400° with decomposition. The substance was insoluble in aqueous or alcoholic alkali and in all organic solvents except hot quinoline. Recrystallized from quinoline and then digested with boiling alcohol for thirty minutes, the **p_2,p_3,p_4-quinquebenzone-p_1,p_5-dicarboxylic acid** formed a colorless powder that sintered at 400° and melted at 405–410° with decomposition.

Anal. Calcd. for $C_{36}H_{22}O_8$: C, 74.2; H, 3.8. Found: C, 74.9; H, 3.9.

Distillation of 0.2 g. of the acid from copper chromite at 10 mm. gave 0.1 g. of **p_2,p_3,p_4-quinquebenzone,** colorless platelets from pyridine, m. p. 285–286°. The same compound was obtained in a yield of 79% from 2 g. of p_2-terbenzone-p_1,p_3-dicarbonyl chloride, 3 g. of aluminum chloride, and excess benzene.

Anal. Calcd. for $C_{34}H_{22}O_4$: C, 82.6; H, 4.5. Found: C, 82.7; H, 4.3.

No pure product (*cyclopentabenzoylene*) other than a minute amount of quinquebenzone, could be isolated from the red liquid that was formed when a mixture of 0.3 g. of p_2,p_3,p_4-quinquebenzone-p_1,p_5-dicarboxylic acid and 0.3 g. of calcium oxide was heated at 390–400°.

Summary

Dibasic acids of the structure $HO(COC_6H_4)_n$-COOH, where n = 3, 4 and 5 and where the phenylene groups are all *para* substituted, have been prepared, but attempts to obtain cyclopolybenzoylenes, $\overline{\lfloor -(COC_6H_4)_n- \rfloor}$, where n = 5, 6 and 8, from them have failed. It is suggested that the dibasic acids have nearly linear structures through resonance of the linking carbonyl groups with the benzene rings.

MINNEAPOLIS, MINNESOTA

RECEIVED SEPTEMBER 17, 1945

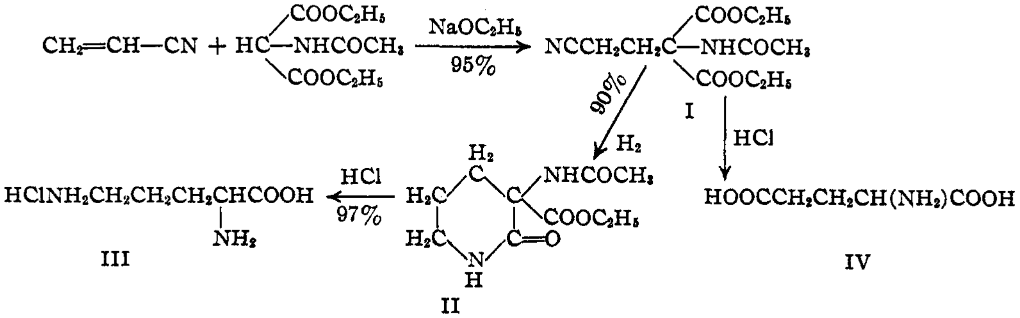
NOTES

A Synthesis of *dl*-Ornithine Hydrochloride

BY N. F. ALBERTSON AND S. ARCHER

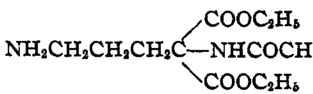
Although several syntheses of ornithine are recorded in the literature, most of them are long and give the final product in small yield. The most recent[1] was patterned after the synthesis of lysine as described by Eck and Marvel.[2] Seven steps were required to give the dibasic amino acid in 12% over-all yield.

A more convenient and economical synthesis, which gave *dl*-ornithine hydrochloride in 83% over-all yield, based on ethyl acetamidomalonate, is illustrated by the following equations



Acrylonitrile was condensed with ethyl acetamidomalonate in the presence of a small quantity of sodium ethylate to give the crystalline ethyl α-acetamido-α-carbethoxy-γ-cyanobutyrate (I) in 95% yield. The structure of the ester was confirmed by hydrolysis with hydrochloric acid to *dl*-glutamic acid in 66% yield. In agreement with Snyder[3] we found that the product resulting from the condensation of methyl acrylate and ethyl acetamidomalonate was a liquid which could be hydrolyzed to *dl*-glutamic acid.

The reduction of I to II was carried out in the presence of Raney nickel catalyst at 68° and 600 lb. of hydrogen. We preferred the piperidone structure for the following reasons. The compound showed no basic properties and the elementary analyses agreed more closely with II than with V. The compound was a nicely



$$NH_2CH_2CH_2CH_2C\begin{matrix}\diagup COOC_2H_5\\ -NHCOCH_3\\ \diagdown COOC_2H_5\end{matrix}$$

V

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[1] Fox, Dunn and Stoddard, *J. Org. Chem.*, **6**, 411 (1941). A bibliography of the earlier work is listed here.

[2] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 76, 74, 374.

[3] Snyder, *et al.*, THIS JOURNAL, **67**, 310 (1945).