the first three fractions indicates that they were probably contaminated by a hydrocarbon produced by the pyrolysis. The first few drops of the forerun burned without the white smoke characteristic of organosilicon compounds.

Treatment of fraction (4) with alcoholic potassium hydroxide caused the rapid evolution of hydrogen. A drop in contact with concentrated aqueous hydrochloric acid set to a gel within five minutes. On standing in a stoppered bottle the constants changed in such a manner as to indicate, by the increasing density, an increase in molecular weight,[4] and, by its decreasing specific refraction, a proportionately smaller change in chemical constitution. It is impossible to state whether this change was spontaneous, or was caused by the traces of hydrogen chloride which are always in the atmosphere of a laboratory where chlorosilanes are frequently about.

Days	n^{20}_D	d^{20}_4	R^{20}_D
0	1.3770	0.9677	0.2377
1	1.3773	.9691	.2375
35	1.3789	.9745	.2371

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[4] The density of polyalkylpolysiloxanes approaches a limiting value with increasing ring size. Hurd (THIS JOURNAL, **68**, 364 (1946)) has demonstrated the additivity of molar volumes in the linear polysiloxanes. The molar volumes of the linear polysiloxanes derived from methyldichlorosilane (ref. 1) provide a molar volume of 58.81 ml. for the CH_3SiHO unit, indicating a limiting density of 1.0219 for $(CH_3SiHO)_\infty$.

RESEARCH LABORATORY
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SCHENECTADY, NEW YORK STUART D. BREWER

RECEIVED JULY 21, 1948

1-Dimethylaminomethyl-2-hydroxydibenzofuran

The Mannich reaction with phenols has been applied to another phenolic derivative, 2-hydroxydibenzofuran. From known preferred orientations in this series,[1] the entering group is assumed to occupy the 1-position.

To 9.2 g. (0.05 mole) of pure 2-hydroxydibenzofuran and 11 ml. (0.056 mole) of 23% aqueous dimethylamine solution dissolved in 50 ml. of ethanol, 4.5 ml. (0.06 mole) of formalin was added dropwise with stirring over a one-hour period. Then the mixture was heated to 90° on the water-bath for one hour and allowed to cool. Beautiful, white crystals deposited, which were filtered off, washed and dried. The yield was 10.5 g. (87.5%) melting sharply at 114–115°.

Anal. Calcd. for $C_{15}H_{15}O_2N$: N, 5.81. Found: N, 5.70.

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[1] Gilman and co-workers, THIS JOURNAL, **56**, 1412 (1934), and thereafter, particularly, Gilman and Van Ess, *ibid.*, **61**, 1365 (1939).

DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE HENRY GILMAN
AMES, IOWA H. SMITH BROADBENT

RECEIVED MAY 10, 1948

2-(*p*-Hydroxyphenyl)-quininic Acid

Application of the Doebner cinchoninic acid synthesis to N-(*p*-hydroxybenzylidene)-*p*-anisidine readily yielded 2-(*p*-hydroxyphenyl)-quininic acid.

N-(*p*-Hydroxybenzylidene)-*p*-anisidine was readily prepared by condensing *p*-hydroxybenzaldehyde and *p*-anisidine in warm ethanolic solution. Melting point, 214–215°.[1]

Pyruvic acid, 34.3 g. (0.44 mole), was slowly dropped into a stirred and refluxing mixture of 97 g. (0.427 mole) of the above-mentioned anil in 1200 ml. of ethanol over a one-hour period. By the time one-half of the pyruvic acid was added, all the anil had gone into solution. The solution was refluxed four hours more, during which time it was concentrated to 300–400 ml. On cooling, a mass of yellowish-red crystals separated, which were filtered off, washed, and dried. The yield was 29 g. (47.2%) of product decomposing *ca.* 305–310°.

Anal. Calcd. for $C_{17}H_{13}O_4N$: N, 4.75. Found: N, 4.76.

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[1] Senier, Forster, *J. Chem. Soc.*, **105**, 2470 (1914).

DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE HENRY GILMAN
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RECEIVED MAY 10, 1948

Phenyl β-D-Galactopyranoside Derivatives[1]

The phenyl β-D-galactopyranoside employed in the following experiments was prepared by catalytic deacetylation with sodium methylate of the carefully purified tetraacetate. The specific rotation[2] of the phenyl galactoside was −41° (*c* 2.3, in water) in agreement with the values which have been reported,[3,4] but the melting point observed in a Pyrex tube or on a heated block[5] was 153–154°, eight degrees higher than the melting point previously reported for this substance.[4] When the melting point was taken in soft glass capillaries lower values were obtained.

Phenyl 4,6-benzylidene-β-D-galactoside was prepared by shaking 8.7 g. of phenyl β-D-galactoside, 25 ml. of freshly distilled benzaldehyde, 15 ml. of anhydrous benzene and 10 g. of fused zinc chloride overnight at room temperature. The product was rinsed exhaustively with water and petroleum ether and recrystallized from alcohol containing a trace of ammonia. The product weighed 9.6 g., melted at 248–249° and had a specific rotation of −116° (*c* 1.2, pyridine). The substance was appreciably hygroscopic. For analysis it was dried in vacuum at 78° over phosphoric anhydride and protected from the atmosphere during weighing and transferring.

Anal. Calcd. $C_{19}H_{20}O_6$ (344.2); C, 66.24; H, 5.87. Found: C, 65.93, 65.97; H, 5.86, 5.90.

Phenyl 2,3-diacetyl-4,6-benzylidene-β-D-galactoside was prepared from the above substance by acetylation with pyridine and acetic anhydride on the steam-bath for one hour. The product crystallized on pouring into water. After recrystallization from alcohol it melted at 171–172°, sp. rot. +43° (*c* 0.8, chloroform).

Anal. Calcd. for $C_{23}H_{24}O_8$ (428.42): C, 64.48; H, 5.65. Found: C, 64.43, 64.46; H, 5.63, 5.68.

Phenyl 2,3-dimethyl-4,6-benzylidene-β-D-galactoside was prepared by methylating 2.5 g. of the benzylidene compound with 25 ml. of methyl iodide, 15 ml. of acetone and 10 g. of silver oxide under reflux with stirring for six hours. After filtration and evaporation of the solvent the residue crystallized, m. p. 163–165°. This substance, recrystallized from alcohol, melted at 165–167°, sp. rot. −38° (*c* 0.83, chloroform).

Anal. Calcd. for $C_{21}H_{24}O_6$ (372.4): C, 67.73; H, 6.50; OCH_3, 16.68. Found: C, 67.46, 67.59; H, 6.65, 6.52; OCH_3, 17.1.

Phenyl 2,3-dimethyl-β-D-galactopyranoside was prepared from 1.8 g. of the above substance dissolved in 25 ml. of boiling acetone by gradually adding 10 ml. of 0.1 *N* aqueous sulfuric acid through the reflux condenser. After

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[1] Contribution from the Southern Regional Research Laboratory, one of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

[2] All optical rotations were measured at 25° with the sodium D line.

[3] B. Helferich, *Ber.*, **77**, 194 (1944).

[4] B. Helferich, R. Gootz and G. Sparmberg, *Z. physiol. Chem.*, **205**, 201 (1932).

[5] Unless otherwise indicated samples were placed between two glass cover slips and melting points were determined between crossed polaroids on a Fisher–Johns apparatus drilled to allow the passage of a 1 mm. beam of light.

a few moments of refluxing, 5 ml. more of acid and 10 ml. of acetone were added and heating was continued for one hour. Then 1 ml. of 5 *N* sulfuric acid and 24 ml. of acetone were added and the solution refluxed for one and one-half hours. The acid was then removed with barium carbonate, and the solution evaporated to dryness *in vacuo.* The residue crystallized and after recrystallization from absolute ether 670 mg. of crystals was obtained; m. p. 93–94°, sp. rot. −39° (*c* 1, chloroform); −31° (*c* 1, water).

Anal. Calcd. for $C_{14}H_{20}O_6$ (284.3): C, 59.14; H, 7.09; OCH_3, 21.83. Found: C, 59.08, 59.19; H, 7.15, 7.19; OCH_3, 22.2.

The position of the methyl groups in this substance (and from this the position of the benzylidene group in the parent substance) was established by hydrolyzing and oxidizing 100 mg. of the substance for four hours at 70–75° with 2 ml. of concentrated nitric acid and 2 ml. of water. Most of the nitric acid was removed by repeated evaporation *in vacuo* with added water. A mixture of nitrophenols was removed by dissolving the sirupy residue in water and extracting with ether. After evaporating the aqueous solution to dryness the residue was esterified by heating in a sealed tube with 1 ml. of hydrogen chloride in methanol (1.25 *N*). The acid was removed with ethereal diazomethane, the solution was evaporated in a current of air, and the residue was distilled in a micro-distillation outfit at 0.2 mm. with a bath temperature of 90–120°. The ester lactone would not crystallize but on treatment with 2 ml. of methylamine in methanol (1 *N*) for two days at roo temperature it yielded the crystalline bismethylamide of 2,3-dimethylmucic acid. The yield of amide after recrystallization from ether was 10 mg., its m. p. was 182–183° not depressed by mixing with an authentic sample. Its specific rotation was −8° (*c* 0.5, water).

An authentic sample of the bismethylamide for comparison with the above substance was prepared from 318 mg. of methyl 2,3-dimethyl-4,6-benzylidene-β-D-galactoside[6] by hydrolyzing and oxidizing with nitric acid in the manner described above. In this instance crystalline methyl 2,3-dimethylmucate lactone (1,4) was obtained from the distillate. Recrystallization from ether gave 56 mg. of substance of m. p. 72–74° (capillary tube or Fisher–Johns) not changed by recrystallization from a mixture of ethyl acetate, ether, and petroleum ether; sp. rot. −54° changing slowly to −7° in water twenty-nine days; bismethylamide, m. p. 184°, sp. rot. −8° (water).

Luckett and Smith[7] have reported a melting point of 92° for methyl 2,3-dimethylmucate lactone (1,4). The present compound may represent a different crystal modification for its melt, on inoculation with an authentic specimen supplied by Professor Fred Smith, crystallized immediately and remelted at the higher temperature. The melting point and rotation of the bismethylamide and the rotation of the lactone ester are in good agreement with the values reported by Luckett and Smith.

Phenyl 2,3-di-N-phenylcarbamyl-4,6-benzylidene-β-D-galactoside was prepared from 9 g. of phenyl benzylidene-β-D-galactoside dissolved in 40 ml. of dry pyridine. Eight ml. of freshly distilled phenyl isocyanate was added; and after the solution had refluxed for one-half hour another 8 ml. of phenyl isocyanate was added and refluxing was continued for one and one-half hours. The volatile material was removed *in vacuo,* finally at a temperature of 100°. The residue crystallized from alcohol and after recrystallization melted at 209°, sp. rot. +47° (*c* 0.67, acetone).

Anal. Calcd. $C_{33}H_{30}O_8N_2$ (582.59): C, 68.03; H, 5.19; N, 4.81. Found: C, 68.22, 67.87; H, 5.20, 5.33; N, 5.26 (av. of 3 Dumas), 5.07 (av. of 4 micro Kjeldahls).

Phenyl 2,3-dibenzyl-4,6-benzylidene-β-D-galactoside was prepared by stirring 12 g. of phenyl diacetylbenzylidene-β-D-galactoside in 180 ml. of xylene with 18 ml. of benzyl chloride and 90 g. of powdered potassium hydroxide on the steam-bath for four hours. The product was recovered by pouring into water and steam distilling until free of volatile materials. The water insoluble residue was rebenzylated as before. The product from the second benzylation crystallized poorly from alcohol, isopropanol, or acetone–petroleum ether. It melted not sharply at about 185–195°, sp. rot. −10° (*c* 1.8, chloroform) and numerous analyses were slightly low in carbon and high in hydrogen. A typical analysis is given.

Anal. Calcd. $C_{33}H_{32}O_6$ (524.59): C, 75.55; H, 6.15. Found: C, 74.64; H, 6.32.

Phenyl 2,3-dibenzyl-β-D-galactopyranoside was prepared by hydrolysis of 4.4 g. of the preceding compound in 85 ml. of acetone and 5 ml. of *N* hydrochloric acid under reflux. After one hour 10 ml. more acid was added and heating continued another hour. The solution was neutralized with aqueous ammonia and evaporated to dryness *in vacuo.* The residue was fractionally crystallized from alcohol and, after removal of a small amount of high-melting material, 1.4 g. of product was obtained. Recrystallization from aqueous acetone yielded a substance melting at 115–117°, sp. rot. −7° (*c* 1.9, pyridine).

Anal. Calcd. $C_{26}H_{28}O_6$ (436.48): C, 71.54; H, 6.47. Found: C, 70.87, 70.85, 70.95; H, 6.46, 6.44, 6.56.

The writer is indebted to Lawrence E. Brown for micro carbon–hydrogen and Dumas nitrogen analyses; to L. W. Mazzeno, Jr., for methoxyl analyses; and to Mrs. V. O. Cirino for micro-Kjeldahl nitrogen analyses.

SOUTHERN REGIONAL RESEARCH LABORATORY
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RECEIVED JUNE 25, 1948

New Compounds for Cancer Research

The following new fluorene derivatives were among others prepared for testing at the Sloan–Kettering Institute under a grant from that foundation.

2-Dimethylaminofluorene.—Eighty grams of 2-aminofluorene, 300 cc. of benzene and 130 cc. of dimethyl sulfate were heated with mechanical stirring on an oil-bath maintained at 140–160° for four hours. After dilution of the mixture with 100 cc. of benzene, the excess dimethyl sulfate was decomposed by the slow addition of 60 g. of sodium hydroxide in 200 cc. of water followed by heating for half an hour. The benzene layer was boiled with Darco, filtered, evaporated to half its volume and cooled. Forty grams of crude 2-dimethylaminofluorene was obtained. This was recrystallized from ethanol (Darco) yielding 20 g. of a faint pinkish-white compound melting at 176°. A sample recrystallized several times from benzene melted at 176–178°.

Anal. Calcd. for $C_{15}H_{15}N$: N, 6.69. Found: N, 6.63.

Diethyl Fluorene-2,7-dicarbamate.—To a mechanically stirred boiling suspension of 9.8 g. of 2,7-diaminofluorene and 6 g. of sodium carbonate in 250 cc. of benzene, 10 cc. of ethyl chlorocarbonate was added dropwise. A white precipitate began forming immediately. Stirring was continued for a short time after all the ethyl chlorocarbonate had been added. After cooling the solid was filtered, washed several times with ether and dried. After recrystallization from xylene 5.2 g. of fluffy, cream-white crystals, m. p. 220–221.5°, was obtained.

Anal. Calcd. for $C_{19}H_{20}O_4N_2$: N, 8.23. Found: N, 8.08.

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RECEIVED AUGUST 5, 1948

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[6] J. W. H. Oldham and D. J. Bell, THIS JOURNAL, **60**, 323 (1938).

[7] S. Luckett and F. Smith, *J. Chem. Soc.*, 1106–1114 (1940).