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

(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
GENERAL ELECTRIC COMPANY
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.

(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°.

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

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

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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

(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.