ture proposed for uroporphyrin.[1] Previous studies have not applied the Willgerodt reaction for the preparation of pyrrole acetic acids.[2,3,4,5] We have used the Willgerodt reaction as described by Schwenk[6] with 2,4-dimethyl-3-acetyl-5-carbethoxypyrrole. It was possible to obtain the thiomorpholide, but not to hydrolyze it to the substituted acetic acid. Vigorous alkaline hydrolysis gave only an amorphous neutral material, perhaps a polymer of 2,3,4-trimethylpyrrole. The thiomorpholide was reduced by Raney nickel to the expected amine.

Experimental

Thiomorpholide from Acetylpyrrole.—To 10.5 g. of 2,4-dimethyl-3-acetyl-5-carbethoxypyrrole was added 4 g. of sulfur and 25 g. of morpholine. The mixture was refluxed for two hours. It was cooled, diluted with water, and extracted with chloroform. The chloroform solution was washed with water, 10% hydrochloric acid, and again with water, dried and distilled to small volume. There crystallized a first crop of 6.2 g. m. p. 171–172°. This was extracted with carbon disulfide to remove sulfur and recrystallized from chloroform–carbon tetrachloride and then from acetone, m. p. 176–177° (178–179° cor.).

Anal. Calcd. for $C_{15}H_{22}N_2O_3S$: C, 58.0; H, 7.15; S, 10.75; N, 9.0. Found: C, 58.3; H, 7.14; S, 10.4; N, 8.7.

The nitrogen and sulfur analyses exclude the possibility that the 5-carbethoxy group underwent aminolysis as occurred with the keto-acids of Schwenk.[6]

A sample of the compound heated on the steam-bath for thirty minutes in 50 cc. of ethanol and 30 cc. of 0.1 *N* sodium hydroxide gave a mixture from which only the starting material was obtained pure. No crystalline product could be obtained when the substance was hydrolyzed by the methods of Schwenk[6] or Newman.[7]

2,4-Dimethyl-5-carbethoxy-3-morpholinoethylpyrrole.—To 500 mg. of the above thiomorpholide was added 150 cc. of boiling absolute ethanol and 50 cc. of a suspension of Raney nickel[8] W-7, containing 7.5 g. of catalyst. The mixture was allowed to stand with occasional shaking for one day. It was filtered and evaporated *in vacuo*. The product was crystallized from ether-pentane, giving 340 mg., m. p. 110–111.5°.

Anal. Calcd. for $C_{15}H_{24}N_2O_3$: C, 64.3; H, 8.63. Found: C, 64.2, 64.3; H, 8.48, 8.60.

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(1) Fischer and Orth, "Die Chemie des Pyrrols," Vol. II, Leipzig, 1937, p. 504.

(2) Ref. 1, Vol. I, p. 260.

(3) Fischer and Müller, *Z. physiol. Chem.*, **246**, 31 (1937).

(4) Fischer and Elhardt, *ibid.*, **257**, 61 (1939).

(5) Fischer, Neumann and Hirschbeck, *ibid.*, **279**, 1 (1943).

(6) Schwenk and Papa, *J. Org. Chem.*, **11**, 798 (1946).

(7) Newman, *ibid.*, **9**, 521 (1944).

(8) Adkins and Billica, THIS JOURNAL, **70**, 695 (1948).

JEFFERSON MEDICAL COLLEGE
PHILADELPHIA, PA.
RECEIVED JULY 7, 1948

NEW COMPOUNDS

N,N-Dicyclohexyl Phthalamide

A solution of 9.9 g. (0.1 mole) of cyclohexylamine in 22.2 g. (0.1 mole) of diethyl phthalate was allowed to stand in a glass-stoppered bottle at room temperature. Crystals were noted at the end of four months. These continued to form slowly. They were filtered off after seven months and washed with dry ether; yield, 0.8936 g., calcd., 16.4 g., 5.4%; the colorless, silky needles did not melt under 300°.

Anal. Calcd. for $C_{20}H_{28}O_2N_2$: N, 8.53. Found: N, 8.4, 8.41.

The substance is soluble in methanol, ethanol, propanol, dioxane, benzene, toluene, chloroform, carbon tetrachloride, formic acid, acetone, methyl ethyl ketone; insoluble in water, heptane, ether, ethyl acetate.

Cyclohexylamine and diethyl phthalate were recovered from the filtrate by distillation under reduced pressure. There was no evidence of the formation of ethyl N-cyclohexylphthalamate.

N-Cyclohexyl phthalimide is known.[1]

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(1) R. W. Wegler and W. Frank, *Ber.*, **70B**, 1279 (1937); Gustave Vanags, *Acta Univ. Latviensis Kim. Facultat.*, Ser. 4, No. 8, 405 (1939); E. H. Gregler and S. I. Gertler, *J. Econ. Entomol.*, **39**, 549 (1946).

SYLVANIA DIVISION
AMERICAN VISCOSE CORPORATION
MARCUS HOOK, PENNSYLVANIA RALPH T. K. CORNWELL
RECEIVED AUGUST 5, 1948

Trimethylcyclotrisiloxane

In an account of the siloxanes derived from methyldichlorosilane[1] the failure to find the cyclic trimer $(CH_3SiHO)_3$, trimethylcyclotrisiloxane, was noted. Since the relative amount of the corresponding derivative of dimethyldichlorosilane is much larger in the thermally rearranged hydrolyzate than in the untreated hydrolyzate,[2] a search for trimethylcyclotrisiloxane in the products obtained by pyrolysis of the hydrolyzate of methyldichlorosilane was indicated. The desired compound was prepared by this method. It is more sensitive toward acid catalyzed rearrangement than is the tetramer, so much so that a molecular weight determination was not attempted. Its molecular weight can be deduced by comparison of its boiling point with those of related compounds.

Procedure.—Thermal rearrangement, by the method of Patnode and Wilcock,[2] of the liquid hydrolysis product,[1] 1216 g., of methyldichlorosilane at 300 to 350° in a stream of nitrogen yielded 1182 g. of distillate. A rough fractionation of this distillate yielded, initially, a fraction of 60 g. boiling below 133°, of which about 40 ml. boiled between 90 and 96°. This fraction, which contained a trace of aqueous acid, was diluted with an equal volume of ether, dried for a few hours over potassium carbonate, and stored in the refrigerator for four days. Upon fractionation none of the trimer was recovered; the first siloxane to distil was the tetramer. The once-cracked oil stock from which the crude trimer had been distilled was again subjected to thermal rearrangement, this time yielding 34 ml. of crude trimer. Fractional distillation yielded, besides some low boiling material, four fractions:

Frac.	B. p., °C.	Vol. cc.	n^{20}_D	d^{20}_4	R^{20}_D
1	92.2–92.6	3.7	1.3745	0.9055	0.2525
2	92.6–93.0	11.7	1.3753	.9242	.2479
3	93.0–93.8	11.6	1.3768	.9528	.2413
4	93.8–93.9	7.3	1.3770	.9677	.2377

Of these, the density and refractive index of fraction (4) were determined immediately after its collection. The constants for the first three fractions are those taken the next day. Their refractive indices were found to have increased slightly overnight. The best specimen was fraction (4) of which the specific refraction is in best agreement with the calculated[3] value of 0.2378. The lower density of

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(1) Sauer, Scheiber and Brewer, THIS JOURNAL, **68**, 962 (1946).

(2) Patnode and Wilcock, *ibid.*, **68**, 358 (1946).

(3) Calculated from the constants of Sauer, THIS JOURNAL, **68**, 954 (1946).

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
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.

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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
AMES, IOWA H. SMITH BROADBENT

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.