ably to the 28% yield of $CF_2BrCH_2CF_2Br$ obtained by adding CF_2Br_2 to 1,1-difluoroethylene.[7]

The Attempted Addition of Bromochlorodifluoromethane to 1-Chloropropene.—The autoclave, charged with the methane derivative (920 g., 5.6 moles), 1-chloropropene (152 g., 20 moles) and benzoyl peroxide (20 g., 0.08 mole), was rocked and heated four hours at 100°. No material boiling higher than the chloropropene was obtained and 918 g. of bromochlorodifluoromethane was recovered.

1-Chloro-1,1-difluorobutane.—A mixture of 3-bromo-1-chloro-1,1-difluorobutane (115 g.), zinc dust (113 g.) and hydrochloric acid (600 ml. of 1.5 molar) was refluxed for several hours. Distillation of the organic product gave two fractions. The first (11 g.) consisted of 1-chloro-1,1-difluorobutane, b.p. 55.5°, n^{25}_D 1.3476. The higher boiling material (18 g.), b.p. 81.2°, n^{25}_D 1.3660, d^{25}_4 1.0647, is believed to be the coupled product $CF_2ClCH_2CH(CH_3)CH(CH_3)CH_2CF_2Cl$.

Anal. Calcd. for $C_8H_{12}Cl_2F_4$: Cl, 27.8. Found: Cl, 27.9.

1-Chloro-1,1-difluoro-3-methylbutane.—A mixture of 3-bromo-1-chloro-1,1-difluoro-3-methylbutane (93 g.), zinc dust (30 g.) and hydrochloric acid (170 ml. of 1.5 molar) was refluxed for six hours. The organic layer was separated and distilled. The reduced compound (34 g.), b.p. 74.5–75.5°, n^{25}_D 1.3665, d^{25}_4 1.064, was obtained in a 65% yield and 10 g. of unreacted starting material was recovered.

1-Chloro-1,1-difluoro-2-methylbutane.—Refluxing the 2-butene adduct (100 g.) with zinc dust (130 g.) and hydrochloric acid (200 ml. of 1.5 molar) gave a 30% yield of $CF_2ClCH(CH_3)CH_2CH_3$. A center fraction of the distilled material had the following properties: b.p. 74.5–75°, n^{25}_D 1.3636, d^{25}_4 1.0487.

Anal. Calcd. for $C_5H_9ClF_2$: Cl, 24.9. Found: Cl, 24.6.

1-Chloro-1,1-difluoro-2-butene.—1,1-Difluoro-1-chloro-3-bromobutane (165 g.) was added dropwise to potassium hydroxide (84 g.) dissolved in isopropyl alcohol (250 cc.) in a liter flask equipped with stirrer, addition funnel and six-inch column with variable take-off head. Reflux was maintained at 75°. The material was removed, washed, dried and fractionated. One fraction of 47 g. was obtained with the following constants: b.p. 59.5–60°, n^{25}_D 1.3656, d^{25}_4 1.1100; MR_D calcd. for $C_4H_5F_2Cl$: 25.07, found 25.17; chlorine analysis calcd. for $C_4H_5F_2Cl$: 28.1, found 26.42. The yield was 46% of the theoretical.

1-Chloro-1,1-difluoro-3-methyl-2-butene.—In the apparatus described above was placed 200 cc. of methanol and potassium hydroxide (28 g.). To this refluxing mixture was added 1,1-difluoro-1-chloro-3-bromo-3-methylbutane (80 g.) dropwise. The olefin resulting was removed, dried and fractionated. The yield of $CF_2ClCH{=}C(CH_3)_2$, b.p. 10–11° (28 mm.) was 78% (39 g.).

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Kolbe Electrolysis of *dl*-α-Bromopropionate in Water

BY G. W. THIESSEN AND R. MILLER[1]

RECEIVED JULY 8, 1954

The electrolysis of potassium *dl*-α-bromopropionate in concentrated aqueous solution yields ethylidene bromide, plus some unidentified material. This is a surprising result. If the general acid R·COOH be converted to a salt and electrolyzed with a smooth platinum anode, the typical products are R·R· (R minus H), R·COO·R, and R·So, So being a radical derived from the solvent anion.[2] Ethylidene bromide is none of these; nor is it the (R minus Br) which might be expected by analogy to (R minus H). Instead it is (R plus Br).

The extra Br gained by R must have come from another R, directly or indirectly. Although the solvent after electrolysis shows much bromide ion, the direct transfer seems likelier, for these reasons: (a) there is practically no H transfer between solvent and R in the electrolysis of acetate to methane[3]; (b) in the electrolysis of acetate to methane at low current densities, the H gained by R comes from another methyl, not the solvent[4]; and (c) in the electrolysis of propionate to ethylene, which is (R minus H), the hydrogen is lost from the β-carbon.[5] Hydrogen (electropositive) lost thus would correspond to bromine (electronegative) lost from the α-carbon.

In presence of excess bromide ions, the efficiency of the electrolysis becomes low, apparently due to the preferential discharge of bromide. This was discovered in an attempt to conserve the potassium ion by replenishing free acid as the electrolysis proceeded; the process was impracticable. This is held as an additional argument against the extra acquired bromine atom being derived from an ion in the solvent. As a further argument in the same direction, the oily yield appears in the first few minutes of electrolysis, before hydrolytic or reductive development of bromide ion in the solvent could have proceeded far.

Experimental

Thirty ml. (51 g., 0.33 g.-mole) of Eastman Kodak Co. *dl*-α-bromopionic acid was mixed, with cooling, with 42 ml. of distilled water and 21 ml. of aqueous saturated (room temperature) potassium hydroxide solution. The anode used was Pt wire approx. 0.17 cm.² surface and the cathode Pt foil, about 1.4 cm.² surface. The temperature in the cell was held to 40° or less by external cooling, the mean current density about 1.2 amp./cm.² at anode and the total throughput, about 0.4 faraday. No diaphragm was used. Excessive temperature or throughput yields free bromine; excess free acid hinders separation of the yield.

The electrolyte soon becomes cloudy and deposits about 3 g. of heavy amber oil. Gases evolve simultaneously, being mostly hydrogen and carbon dioxide in about equal amounts; a few per cent. of oxygen may appear, with traces at most of carbon monoxide and unsaturates. The yield from several electrolyses is united to form a working crude sample. Washing with cold concd. sulfuric acid yields a portion more dense than the acid, which boils in the neighborhood of 105° with some decomposition to produce HBr. Its density is 2.03, n^{25}_D 1.515, 84.9% Br; for ethylidene bromide, the b.p. is 108–110°, density 2.05, n^{25}_D 1.513, 85.1% Br. No satisfactory derivative for ethylidene bromide was found recorded.

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[1] Assistance from the Research Corporation is gratefully acknowledged.

[2] G. Thiessen, *Trans. Ill. Acad. Sci.*, **43**, 77 (1950).

[3] H. Erlenmeyer and W. Schoenauer, *Helv. Chim. Acta*, **20**, 222 (1937).

[4] K. Clusius and W. Schanzer, *Z. physik. Chem.*, **A192**, 273 (1943).

[5] W. Schanzer and P. Kruis, *ibid.*, **A191**, 301 (1942).

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Phenylsilanetriol

BY LESLIE J. TYLER

RECEIVED AUGUST 27, 1954

Previous investigators[1,2] have made use of the hydrolysis of alkoxysilanes with distilled water to prepare the corresponding hydroxy compounds. These mild conditions allow the isolation of un-

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[1] J. F. Hyde, THIS JOURNAL, **75**, 2166 (1953).

[2] S. W. Kantor, *ibid.*, **75**, 2712 (1953).

stable silanols such as dimethylsilanediol. The latter compound was prepared by Hyde using a cold hydrolysis of dimethyldiethoxysilane and by Kantor using a hot hydrolysis of dimethyldimethoxysilane. Kantor hydrolyzed phenyltrimethoxysilane with distilled water at reflux temperature to obtain a low polymer phenylpolysiloxane.

Prior to Kantor's publication it was found in this Laboratory that the hydrolysis of phenyltrimethoxysilane at lower temperatures gave a good yield of phenylsilanetriol. The hydrolysis is accomplished best at temperatures near 10° although temperatures as high as 40° can be used. An acid catalyst facilitates the hydrolysis at low temperatures and 0.5% acetic acid was found quite satisfactory. The hydrolysis can be performed more slowly using distilled water.

As would be expected the compound is not very stable. It decomposes on heating and is sensitive to alkali and acid catalysts. On standing in sealed containers some samples have gradually resinified with loss of water although a few samples have been stored for over a year with no outward signs of decomposition and with only a slight drop in melting point. The melting point (or decomposition point) was difficult to determine and appeared to be a function of time *vs.* temperature. Determining the melting points in Pyrex capillary tubes using a rate of heating of 3° a minute gave consistent results on freshly prepared samples. The compound melted 128–130°.

Phenylsilanetriol crystallizes during its preparation in the form of flat, shiny, white platelets. It is slightly soluble in water, is somewhat more soluble in methanol and acetone, and is insoluble in toluene and petroleum ether. It is very unstable in solution. Dilute aqueous solutions become milky in less than an hour and all attempts to purify the compound by recrystallization led to complete loss of the material due to condensation or resulted in a product with a lower melting point and a more pronounced tendency to decompose on standing. The triol decomposes on melting with loss of water to give a resinous product which is toluene soluble. If heated further this resin condenses to an insoluble, hard gel.

Experimental

Hydrolysis of Phenyltrimethoxysilane.—Into a one-liter, three-necked flask was placed 198 g. (1.0 mole) of phenyltrimethoxysilane (b.p. 108° (20 mm.), $n^{25}\mathrm{D}$ 1.4701, $d^{25}{}_{25}$ 1.067). To this was added 108 g. of 0.5% acetic acid. The mixture was cooled to 10° and agitated thoroughly for four hours. During this period a white, crystalline material precipitated gradually and the liquid phase became homogeneous. The mixture was cooled to −20° and then filtered. The crystals which were obtained were washed once with distilled water and allowed to dry overnight at room temperature. The product weighed 117 g. (0.75 mole), a 75% yield of phenylsilanetriol.

Anal. Calcd. for $SiC_6H_8O_3$: Si, 17.9; OH, 32.7. Found: Si, 17.56, 17.55; OH, 32.5, 32.9.

In determining the hydroxyl content it was found that the Zerewitinoff technique gave erratic results due to gel formation. The analyses were made by condensing the triol in xylene at reflux temperature using a trace of KOH as catalyst. The water evolved was measured by collection in a Dean–Stark water trap. Fairly large (50 g.) samples were used for maximum accuracy.

The infrared spectrum of phenylsilanetriol shows absorption maxima at wave lengths of 3.15, 7.01, 8.82, 11.03, 13.50 and 14.35 μ. Bands at 6.3, 7.0, 8.8, 13.5 and 14.3 μ are characteristic of a single phenyl group on silicon. The 3.15 band is the stretching mode of the strongly associated hydroxyl and the OH bending vibrations lie between 10.5 and 12 μ. The sample was run using the KBr pressed pellet technique.

The author wishes to thank Dr. J. F. Hyde for suggestions and advice and Dr. A. L. Smith for the infrared spectrum and analysis.

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Studies on Pituitary Adrenocorticotropin. X. Further Sequences Near the N-Terminus of Corticotropin-A

BY W. F. WHITE AND W. A. LANDMANN

RECEIVED AUGUST 2, 1954

In a previous communication[1] it was reported that serine and tyrosine comprise the first two amino acids at the N-terminus of corticotropin-A. A systematic study of the fragments produced by enzymatic hydrolysis of corticotropin-A has led to the recognition of the seven peptide fragments listed in Table I. The cumulative evidence obtained from these peptides (as shown in the table) is best explained by the sequence: Ser·Tyr·Ser·Met·Glu·His·Phe·Arg. . .[2,3]

Peptides no. 1, 2, 5 and 7 are primary ones, being formed by direct treatment of corticotropin-A with crystalline enzymes. Of the remaining peptides, no. 3 and 4 are formed by secondary hydrolysis of the large fragment[4] remaining after long-term peptic hydrolysis of corticotropin-A. Present evidence indicates that such peptic hydrolysis removes a total of eleven amino acid residues from the carboxyl end of corticotropin-A, in addition to the five amino acid residues from the amino end comprising peptide no. 5.

The first two positions in the amino acid chain of corticotropin-A were clear from early work on the intact molecule[1] and the sixth, seventh and eighth positions were obtained by a consideration of peptides no. 2, 3, 4, 5 and 7. An attempt was made to fix the third, fourth and fifth positions by treatment of peptide no. 5 with carboxypeptidase. However, the rate of splitting of glutamic acid proved to be the limiting factor in the reaction. As a consequence, it was not possible to determine the sequence even though the peptide was almost completely split into its constituent amino acids after 24 hours.

The third position was finally determined by treatment of peptide No. 2 with dinitrofluoroben-

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(1) W. A. Landmann, M. P. Drake and W. F. White, THIS JOURNAL, **75**, 4370 (1953).

(2) With one omission this sequence was proposed tentatively in a paper by E. E. Hays and W. F. White presented at the Laurentian Hormone Conference, Sept. 9, 1953. Most of the work up to that time had been done with the peptic and tryptic fragments, and the second serine was not discovered until the chymotryptic fragments were studied in detail. The Laurentian paper is published in "Recent Progress in Hormone Research," V. IX, Academic Press, New York, N. Y., 1954.

(3) In a recent paper (THIS JOURNAL, **76**, 3607 (1954)), Harris and Li have shown that the first seven amino acids of α-corticotropin (sheep origin) are the same as we have found for corticotropin-A (hog origin).

(4) W. F. White, THIS JOURNAL, **76**, 4194 (1954).