zothiophene-5-dioxide sample was prepared by H. A. Pacevitz.[8]

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(8) H. Gilman, A. L. Jacoby and H. A. Pacevitz, *J. Org. Chem.*, **3**, 120 (1938).

DEPARTMENT OF CHEMISTRY
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Pentamethyl and Triacetyl Derivatives of *myo*-Inositol[1]

BY G. E. MCCASLAND AND STEPHEN BOUTSICARIS

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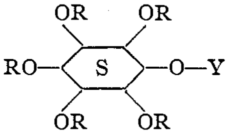
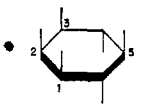
To facilitate another investigation which is still in progress we have prepared the partially alkylated or acylated inositols described below.

In 1947 McGowan[2] reported the preparation of the first pentamethyl ether of *myo*-inositol (I, R = CH_3, Y = H). His product was a sirup but did



I



II

yield a crystalline monoacetate of m.p. 101°. By saponification of this monoacetate we have now obtained the pentamethyl ether itself in crystalline form, m.p. 51°. We have further characterized the ether by converting it to its monobenzoate, m.p. 133°.

Such a pentaalkyl ether (or its monoester) can have only a single structure I, but twenty diastereomers are possible. However, the configuration II of the starting material here used limits the possible diastereomers to four, since no inversions of configuration would be expected.

In 1915 Griffin and Nelson[3] reported a procedure for conversion of *myo*-inositol to acetylated mono- and dimethyl ethers. While repeating this procedure we isolated a previously unreported by-product of m.p. 71°. This compound is apparently the first crystalline triacetate[4] of *myo*-inositol, as indicated by its analysis, and its transformation into the known hexaacetate on further acetylation.

Three structures are possible for an inositol triacetate, and ten diastereometric configurations are probable when the starting material II is used.

Each product here reported appears to consist of a single pure isomer, but the configurations (and structure for the triacetate) remain undetermined.

Experimental

M.p.'s (corrected) were taken on Köfler micro-block; microanalyses by Mr. R. S. Pyke.

***myo*-Inositol Pentamethyl Ether Monoacetate of M.P. 101°.**—Fifty grams of anhydrous *myo*-inositol when methylated by the procedure of West and Holden,[5] as modified by McGowan,[2] gave 10 g. of crude pentamethyl ether (colorless sirup, b.p. 123–145° (150 μ)), which on acetylation as described[2] gave 7.0 g. (22%) of the pentamethyl monoacetate, m.p. 100–101° (reported[2] 101°).

***myo*-Inositol Pentamethyl Ether of M.P. 51°.**—A solution of the pentamethyl ether monoacetate (7.0 g.) in 140 ml. of 1 *N* sodium hydroxide was kept at 25° for one hour, then neutralized with 12 *M* hydrochloric acid. The solution was saturated with potassium carbonate and extracted repeatedly with chloroform. The dried extract on evaporation left 6.0 g. of brown sirupy residue, which on vacuum-distillation gave 3.0 g. of a colorless viscous sirup, b.p. 127° (150 μ). The sirup solidified on standing overnight at 5°. The solid product was recrystallized twice from ligroin (b.p. 80–100°) giving 2.5 g. (42%) of ***myo*-inositol pentamethyl ether**, colorless crystals, m.p. 50–51°. The crystals are soluble in water, alcohol, or benzene.

Anal. Calcd. for $C_{11}H_{22}O_6$: C, 52.78; H, 8.86. Found: C, 52.38; H, 8.49.

On reacetylation of the crystalline pentamethyl ether, the monoacetate of m.p. 101° was again obtained.

***myo*-Inositol Pentamethyl Ether Monobenzoate of M.P. 133°.**—To the pentamethyl ether (0.60 g.) in 3.0 ml. of dry pyridine was added with stirring 0.50 ml. of benzoyl chloride. After five minutes the crystals which had separated were collected, washed with water, with 0.5 *M* sodium carbonate, and again with water, and dried. By recrystallization from ligroin, 0.65 g. (76%) of ***myo*-inositol pentamethyl ether monobenzoate**, colorless crystals, m.p. 132–133°, were obtained. The crystals are soluble in alcohol or benzene.

Anal. Calcd. for $C_{18}H_{26}O_7$: C, 61.00; H, 7.40. Found: C, 60.99; H, 7.31.

***myo*-Inositol Triacetate of M.P. 71°.**—*myo*-Inositol (20 g.) was treated by the methylation and acetylation procedure[3] of Griffin and Nelson. The filtered ethereal mother liquors, from which the acetylated mono- and dimethyl ethers had already crystallized, on long standing formed a third crop of crystals. This third crop was recrystallized from ethanol, giving 0.30 g. (0.8%) of colorless crystals, m.p. 70–71°. The crystals are soluble in chloroform but not in water. Analysis indicates that the new compound is a triacetate of (unmethylated) *myo*-inositol.

Anal. Calcd. for $C_{12}H_{18}O_9$: C, 47.06; H, 5.92. Found: C, 47.49; H, 5.89.

The triacetate (0.27 g.) on further acetylation with 5 ml. of hot acetic anhydride containing 0.1 g. of zinc chloride gave the expected *myo*-inositol hexaacetate (0.30 g., 79%) of m.p. 212–213° (reported[6] 211–212°).

Although the use of methylating agents in the procedure may seem superfluous, no more direct method for preparing this triacetate has yet been found.

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[1] Aided by a grant from the Research Council of Ontario.

[2] J. C. McGowan, *J. Soc. Chem. Ind.*, **66**, 446 (1947).

[3] E. Griffin and G. Nelson, THIS JOURNAL, **37**, 1566 (1915).

[4] The only previously reported triacetate of *myo*-inositol was an amorphous, gummy, hygroscopic substance of unstated m.p. and uncertain purity. See H. Müller, *J. Chem. Soc.*, **101**, 1781 (1912).

[5] E. S. West and R. F. Holden, *Org. Syntheses*, **20**, 97 (1940).

[6] L. Maquenne, *Ann. Chim.*, [6] **12**, 100 (1887).

CHEMISTRY DEPARTMENT
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Antimony(III) Fluoride–Dioxane Addition Compound[1]

BY H. M. HAENDLER, R. H. GLAZIER AND D. W. BRECK

RECEIVED APRIL 8, 1953

Antimony(III) fluoride, which is reported to occur as a molecular crystal,[2] does not show the tendency to form addition compounds with many organic compounds that is so characteristic of the other halides of antimony(III). Solubility measurements in various organic solvents,[3] such as benzene or chlorobenzene, gave no indication of reaction. There was, however, some evidence of reac-

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[1] This research was supported by the Research Corporation and is taken in part from the M.S. thesis of R. H. Glazier.

[2] A. Byström and A. Westgren, *Arkiv. Kemi, Mineral Geol.*, **17B**, No. 2, 1 (1943); R. W. G. Wyckoff, "Crystal Structures," Interscience Publishers, Inc., New York, N. Y., 1951, Chap. V, table p. 17b.

[3] D. W. Breck, J. L. Harvey and H. M. Haendler, *J. Phys. Colloid Chem.*, **53**, 906 (1949).

tion with 1,4-dioxane, which has frequently been used with other halides.[4]

Subsequent study has shown the formation of a 1:1 addition compound by direct reaction of antimony(III) fluoride and dioxane and by reaction in methanol solution. The complex decomposes at 143° into its components and can be used as a mild fluorinating agent.

Experimental

Antimony(III) fluoride was refluxed for 15 minutes with a 14-fold excess of dioxane, filtered and cooled. Alternatively, a mixture of 15 ml. of dioxane (0.17 mole) and 15 ml. of methanol was added slowly to a solution of 19.3 g. (0.11 mole) of the fluoride in 30 ml. of methanol. After brief refluxing the solution was cooled, the crystals removed, and dried in a stream of dry air. Samples were analyzed for antimony by titration with potassium bromate,[5] using Naphthol Blue Black.[6]

Anal. Calcd. for $SbF_3 \cdot C_4H_8O_2$: Sb, 45.62. Found: Sb, 45.47, 45.54, 45.57.

The dissociation temperature was found by determining the heating curve of a 14-g. sample in a nickel cell, using copper–constantan thermocouples and a Speedomax recorder. A sharp break occurred at 143°, and a sample heated to 305° showed a break in its cooling curve at 290°, corresponding to the m.p. of the fluoride.

Benzotrichloride was fluorinated by the complex, using the apparatus and procedures given by Henne,[7] maintaining the same fluoride–chloride ratio. Both benzotrifluoride and the chlorodifluoride were formed.

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(4) M. S. Kennard and P. A. McCusker, This Journal, **70**, 1039 (1948); C. J. Kelley and P. A. McCusker, *ibid.*, **65**, 1307 (1943).

(5) H. H. Willard and H. Diehl, "Advanced Quantitative Analysis," D. Van Nostrand Publishing Co., Inc., New York, N. Y., 1943, p. 350.

(6) G. F. Smith and R. L. May, *Ind. Eng. Chem., Anal. Ed.*, **13**, 460 (1941).

(7) A. L. Henne in R. Adams, ed., "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 62.

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Ammonium Pentafluorozirconate(IV) and its Monohydrate[1]

BY HELMUT M. HAENDLER AND DEAN W. ROBINSON

RECEIVED APRIL 8, 1953

Ammonium pentafluorozirconate(IV), NH_4ZrF_5, has been reported as one of the intermediate products of the thermal decomposition of ammonium heptafluorozirconate(IV), $(NH_4)_3ZrF_7$.[2] Attempts to grow single crystals of the pentafluorozirconate from solution for X-ray structural studies led to the discovery of its monohydrate. Both compounds crystallize from a solution of zirconium oxide in hydrofluoric acid, to which has been added 75% of the theoretical quantity of ammonium fluoride. The predominant product is controlled by the rate of crystallization. Rapid crystallization favors formation of the hydrate, slow crystallization suppresses it. The monohydrate loses water spontaneously in air of low humidity to become the anhydrous compound. Powder diffraction and Weissenberg photographs of the two compounds are distinctive.

Experimental

All crystallizations were carried out with platinum or polyethylene apparatus. To obtain the monohydrate, the solution was evaporated by heating to incipient crystallization, filtered and cooled. The hydrate crystallized in clusters of clear, colorless, six-sided right prisms. These were separated mechanically from the small crystals of the anhydrous compound, the formation of which could not be prevented completely.

Anhydrous pentafluorozirconate was produced with exclusion of hydrate by allowing the solution to evaporate slowly for 2–3 weeks, or by adding a small amount of ethanol prior to the slow evaporation. This compound crystallized in small, colorless, almost square plates, with truncated faces.

X-Ray diffraction powder photographs were taken of the products obtained by heating the hydrate at 110° and from its spontaneous decomposition in air. They were identical with the pattern of the pentafluorozirconate produced in the thermal decomposition of the heptafluorozirconate.

Ammonium ion was determined by distillation from basic solution into boric acid and titration with hydrochloric acid. Zirconium was determined by digestion with sulfuric acid and ignition to the oxide. Water was determined by heating at 110°.

Anal. Calcd. for $NH_4ZrF_5 \cdot H_2O$: NH_4, 8.12; Zr, 40.94; H_2O, 8.10. Found: NH_4, 7.64; Zr, 41.15; H_2O, 8.25.

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(1) Research supported by the Atomic Energy Commission and the Research Corporation.

(2) H. M. Haendler, C. M. Wheeler and D. W. Robinson, This Journal, **74**, 2352 (1952).

Diazonium Fluoborates as Initiators of Vinyl Polymerization[1]

BY C. S. MARVEL, H. Z. FRIEDLANDER, SHERLOCK SWANN, JR., AND H. K. INSKIP

RECEIVED JANUARY 26, 1953

In some experiments on the electrolytic generation of free radicals for the initiation of polymerization,[2] hydroquinone was added as a "shortstop" immediately after the electrolysis to prevent polymerization during the examination of the mixture. In those runs involving the electrolysis of *p*-bromobenzenediazonium fluoborate, extensive polymerization of acrylonitrile was observed after the addition of hydroquinone, but not before. Tests showed that the sulfuric acid anolyte solution and the fluoborate anion were not responsible for the polymerization. Further study demonstrated that the diazonium fluoborate in the presence of hydroquinone or ferrous ammonium sulfate caused the initiation of polymerization at 30°. In Table I are summarized the results of a number of homopolymerizations and copolymerizations initiated by substituted benzenediazonium fluoborates.

The effect of *p*H on yield and viscosity of polyacrylonitrile is demonstrated in experiments 1–6. Optimum conditions obtain at about *p*H 3. At 0° no polymer was obtained from acrylonitrile even after four days (experiments 7, 8) unless the amount of initiator was doubled over that used at 30° (experiments 9–14), and even with increase of initiator the yield and viscosity were relatively low. The effectiveness of the ferrous-salt activator in promoting polymerization of acrylonitrile at 30° is demonstrated in the 18-hour polymerizations (ex-

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(1) The work discussed herein was performed as a part of the research project sponsored by the Reconstruction Finance Corporation, Office of Synthetic Rubber, in connection with the Government Synthetic Rubber Program.

(2) H. Z. Friedlander, S. Swann, Jr., and C. S. Marvel, *J. Electrochem. Soc.*, in press.