process[2] has made available for chemical studies many compounds whose structures would be quite difficult to duplicate by conventional synthetic methods. Undecafluorocyclohexanecarboxylic acid is such a compound. The physical constants of this acid and its preparation have been reported by Kauck and Diesslin.[3]

The silver salt can be prepared by dissolving the acid in a neutral fluorocarbon derivative, $(C_4F_9)_2O$ for example, and treating the solution with silver oxide. The lack of acid or base character of the fluorocarbons and many of their derivatives makes them ideal for use as reaction media in many experiments. The procedure is needed because $C_6F_{11}CO_2H$ is unstable in aqueous solution so that it has not been feasible to prepare the silver salt by a wet method. Once formed, the silver salt is a stable, non-hygroscopic, crystalline solid. It is a suitable intermediate in the preparation of the cyclic monobromide and monoiodide, $C_6F_{11}Br$ and $C_6F_{11}I$. These compounds were prepared by treating with an excess of dry halogen a suspension of the silver salt in $(C_4F_9)_3N$, an inert, high boiling (175°) liquid. The procedure is one developed in these laboratories[4] and is similar to those reported by Henne and Finnegan[5] and Haszeldine.[6]

Experimental

The Preparation of $C_6F_{11}CO_2Ag$.—Several preparations of the salt were carried out, all characterized by high yields of the desired product. In a typical experiment 9.049 g. of the acid was dissolved in 66 cc. of $(C_4F_9)_2O$ to form a very slightly cloudy solution. There was added to the solution 3.217 g. of dry, powdered, alkali-free silver oxide and the mixture set aside in the dark. After three days of intermittent shaking, reaction appeared to have stopped and only a trace of unreacted silver oxide was visible. The silver salt, 11.345 g. (94.3% yield), was collected on a sintered Pyrex filter cone, washed with $(C_4F_9)_2O$ and dried at 50° for ten hours. The washings gave no further reaction with silver oxide.

The salt was obtained as a fine, white crystalline material, rather waxy in texture. It is not hygroscopic, but is quite soluble in water. Silver salts of fluorocarbon carboxylic acids are usually quite light sensitive and all operations in its preparation were carried out in a dark room. *Anal.* Found: Ag, 25.17. Calcd. for $C_6F_{11}CO_2Ag$: Ag, 24.93.

The Preparation of $C_6F_{11}Br$.—In this experiment 10.0 g. of $C_6F_{11}CO_2Ag$ (0.023 mole) was suspended in 50 cc. of $(C_4F_9)_3N$ and treated with 7.0 g. (0.044 mole) of dry bromine at *ca.* 60–70°. There was isolated 4.5 g. (54%) of $C_6F_{11}Br$, b.p. 90–92° at *ca.* 735 mm., $n^{20}D$ 1.3205. *Anal.* Found: mol. wt., 352, 362 (vapor density); F, 57.2, 56.8; Br, 22.0. Calcd. for $C_6F_{11}Br$: mol. wt., 361; F, 57.9; Br, 22.1.

The Preparation of $C_6F_{11}I$.—A suspension of 9.9 g. (0.023 mole) of $C_6F_{11}CO_2Ag$ in 50 cc. of $(C_4F_9)_3N$ was treated with 12.6 g. (0.05 mole) of dry iodine at temperatures up to *ca.* 170°. There was isolated from the reaction products 7.7 g. of crude $C_6F_{11}I$ and, after fractionation, 5.9 g. (63% yield) of good material; b.p. 109–112° (736 mm.), $n^{20}D$ 1.3540. *Anal.* Found: F, 51.1, 49.8. Calcd. for $C_6F_{11}I$: F, 51.2. Both $C_6F_{11}Br$ and $C_6F_{11}I$ are dense, colorless liquids. $C_6F_{11}I$ is sensitive to sunlight and was stored in the dark over mercury.

Acknowledgment.—We would like to thank Dr. H. M. Scholberg and Mr. E. A. Kauck of the Central Research Department of Minnesota Mining & Manufacturing Company for supplying the undecafluorocyclohexanecarboxylic acid used in these experiments.

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Fluorocarbon Chemistry. V. The Decomposition of Undecafluorocyclohexanecarboxylic Acid in Aqueous Solution

BY THOMAS J. BRICE[1a] AND J. H. SIMONS[1b]

The preparation of undecafluorocyclohexanecarboxylic acid has been reported by Kauck and Diesslin.[2]

This acid has many of the physical and chemical properties to be expected by analogy with previously known fluorocarbon acids. It has, in addition, some distinctive properties of its own. A preliminary report on its behavior in aqueous solution is here presented.

We have found that $C_6F_{11}CO_2H$ undergoes a slow decomposition, even at room temperature, when dissolved in water. This is a reaction that does not occur with the known primary straight chain fluorocarbon acids. At room temperature the reaction appears to be complete, as measured by the rate of formation of fluoride ion and water-insoluble fluorocarbons, within seven days. The products are complex and demonstrate that, although the conditions used appear to be quite mild, very far reaching disturbances in the acid molecules are produced. These products are made up largely of water-insoluble neutral fluorocarbons and fluoride ion.

The water insoluble fluorocarbon products consist of compounds containing either six carbon atoms per molecule or of compounds containing about twelve carbon atoms per molecule. Compounds containing less than six or from seven to eleven carbon atoms can be present only in small amount, if at all. The substances found are evidently derived from a single six carbon ring or from the coupling of two such rings.

In an experiment carried out with 33.4 g. of acid the yield of fluorocarbons was 87%. The yield of C_6 compounds was 60% of which half was decafluorocyclohexene. The other C_6 compounds have not been identified but are known to contain little, if any, c-$C_6F_{11}H$. The C_{12} compounds were obtained in about 10% yield. The remaining 17% was contained in intercuts.

Since the yield of decafluorocyclohexene is at least 30%, the process of dissolving the acid in water and allowing it to stand is a suitable preparative method for this compound.

Decafluorocyclohexene has the following physical properties: b.p. 51–52° (728 mm.); $n^{20}D$ 1.292–1.293. *Anal.* Found: mol. wt., 265, 266; F, 71.7, 72.4. Calcd. for C_6F_{10}: mol. wt., 262; F, 72.5.

The double bond in C_6F_{10} is less reactive than those in tetrafluoroethylene and hexafluoropropylene. C_6F_{10} did not add bromine even at 95°, but could be chlorinated photochemically and decolorized neutral permanganate. The photochemical chlorination of 1.4 g. of C_6F_{10} produced $C_6F_{10}Cl_2$ in 62% yield. The dichloride was found to boil at 108° (micro), m.p. 18.5 to 20°, $n^{20}D$ 1.338–1.339. The

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[2] E. A. Kauck and A. R. Diesslin, 116th A.C.S. Meeting, Atlantic City, N. J., September, 1949.

noticeable melting point range suggests that there is still some impurity present or that the product is not a single isomer. *Anal.* Found: F, 55.7, 56.0; Cl, 20.0. Calcd. for $C_6F_{10}Cl_2$: F, 57.0; Cl, 21.3. The literature values reported for this compound are: b.p. 107.5–107.7°; m.p. 12–14°; $n^{20}D$ 1.3413.[3]

The compound or compounds containing approximately twelve carbon atoms per molecule have thus far been obtained only in small amounts and have not been identified. The fraction does decolorize neutral permanganate and can be chlorinated photochemically, indicating olefinic character.

Some preliminary kinetic data indicate that, in general, the acid takes part in reactions at room temperature in the presence of Lewis-type bases both in aqueous and nonaqueous media. The decomposition in water may be considered as an example of this general type of reaction which the acid will undergo.

Acknowledgment.—We would like to thank Dr. H. M. Scholberg and Mr. E. A. Kauck of the Central Research Department of Minnesota Mining & Manufacturing Company for supplying the fluorocarbon acid.

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RECEIVED MARCH 17, 1951

Isolation of Tomatidine from the Roots of the Rutgers Tomato Plant

BY NORMAN G. BRINK AND KARL FOLKERS

Tomatidine, the nitrogenous aglycone of the antifungal agent tomatine, has been isolated directly from the roots of the Rutgers tomato plant (*Lycopersicum esculentum* (L.) Mill., horticultural variety "Rutgers").

The isolation of crystalline tomatine from the dry leaves of the Red Currant tomato, *L. pimpinellifolium*, was described by Fontaine, Irving, Ma, Poole and Doolittle.[1] The isolation of tomatine from the leaves of six species of wild tomato plants was reported by Kuhn, Löw and Gauhe[2] who cited yields of the crystalline product from the dried plant material which varied from 0.5 to 5%, the highest yield being obtained from *L. esculentum var. pruniforme.* They stated that tomatine could not be isolated from the commonly cultivated tomato plants; and that in those plants which did contain it, the amount of tomatine present decreased significantly in September and October.

Acid hydrolysis of crystalline tomatine gave xylose, galactose, two moles of glucose,[3] and a nitrogenous aglycone, tomatidine.[1,2] Recent work[4,5] has shown that tomatidine is a steroid secondary amine, for which the molecular formula $C_{27}H_{45}NO_2$ was proposed. Kuhn, Löw and Gauhe,[2] however, indicated formulas for tomatine and tomatidine containing two less hydrogen atoms.

We wish to report the isolation of tomatidine hydrochloride directly from the roots of the Rutgers tomato plant, a horticultural variety of *L. esculentum* (L.) Mill. developed by L. G. Schermerhorn at the New Jersey Agricultural Experiment Station, and distributed generally about 1934. The plants were gathered during the fall of the year, after the fruit had been picked, and only the washed and dried roots were used in the extraction. The extract was divided into a number of fractions, one of which gave a crystalline product in low yield (*ca.* 0.01%), which after purification was identified as tomatidine hydrochloride. The low yield may be explained partly by the isolation procedure, which included no deliberate acid hydrolytic step; and partly by the fact that the plants were gathered at the time when their tomatine content might be expected[2] to be low.

It is of interest that our analytical results on purified tomatidine hydrochloride are in agreement with the composition $C_{27}H_{45}NO_2$[4,5] rather than $C_{27}H_{43}NO_2$.[2]

Experimental[6]

In a typical extraction procedure, 1.36 kg. of dried root material was moistened with water and then extracted in a Soxhlet apparatus for 24 hours with 15 l. of methanol. The extraction was then continued for an additional three days, using fresh methanol. The combined methanolic solutions were concentrated *in vacuo* to a volume of 300 ml., and to this aqueous solution another 300 ml. of water was added, and the *p*H was adjusted to 8 with sodium hydroxide. After standing with occasional stirring for several days, the mixture was extracted with eight 1-l. portions of ether. The combined ethereal extracts were evaporated and the residue triturated with 2.5 l. of ether. After removal of solids, the ethereal solution was washed with eight 250-ml. portions of very dilute sodium hydroxide solution (*p*H 10); and then it was extracted with eight 250-ml. portions of 0.06 *N* hydrochloric acid. On standing in the cold, the acidic solution deposited crystalline material which was collected by filtration, washed with water, and dried. It weighed 183 mg.

The product, after two recrystallizations from ethanol melted at 275–280° (dec.); $[\alpha]^{25}D$ $-8.8 \pm 2.1°$ (*c*, 0.455 in methanol).

Anal. Calcd. for $C_{27}H_{45}NO_2 \cdot HCl$: C, 71.73; H, 10.26; N, 3.10; Cl, 7.84. Calcd. for $C_{27}H_{43}NO_2 \cdot HCl$: C, 72.05; H, 9.86; N, 3.11; Cl, 7.88. Found: C, 71.76, 71.41; H, 10.26, 10.23; N, 3.50; Cl, 7.83.

Treatment of the recrystallized hydrochloride in methanolic solution with silver oxide, and recrystallization of the product from aqueous ethanol gave the free base, m.p. 204–205°. When this material was admixed with a sample of authentic tomatidine[7] for which we observed the m.p. 205–207°, no depression of the melting point occurred.

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(6) The authors wish to thank Mr. John Madas for technical assistance. They are indebted to Mr. Richard N. Boos and his associates for the microanalyses.

(7) Kindly furnished by Dr. T. D. Fontaine.

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Some Derivatives of 2- and 3-Methylthiophene

BY TOD W. CAMPBELL AND WARREN W. KAEDING

In view of recent reports by various workers on the halogenation of methylthiophenes with N-bromosuccinimide[1a,b,2] we feel that it would be worthwhile to record some of our experimental observations on this reaction, carried out prior to the ap-

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