

tion. The solution was then cooled and extracted with ether to remove unchanged quinaldine. The aqueous layer was made basic and the oil which separated was extracted with ether and dried over sodium sulfate. After removal of the ether, the residue was distilled using a Fenske column. In addition to a small forerun of I, there was obtained 68.5 g. (38%) of a light yellow oil; b.p. 139–145° at 2 mm., n_D^{20} 1.5653.

Anal. Calcd. for $C_{16}H_{23}N_3$: C, 74.66; H, 9.01. Found: C, 74.20; H, 8.95.

The mono-styphnate of VI crystallized from an alcohol-water mixture as yellow needles, m.p. 160–161° dec.

Anal. Calcd. for $C_{22}H_{26}N_6O_3$: C, 52.58; H, 5.22. Found: C, 52.90; H, 5.45.

The di-methiodide of VI was obtained from absolute alcohol as white crystals, m.p. 230–231° dec.

Anal. Calcd. for $C_{18}H_{29}N_3I_2$: C, 39.94; H, 5.40. Found: C, 39.52; H, 5.71.

Diethyl β -(2-Quinoly)-ethylmalonate (II).—A solution, prepared by adding 9.7 g. of dimethyl sulfate in the cold to 15.4 g. of I dissolved in 50 ml. of absolute alcohol, was added dropwise with stirring to a mixture of 49.3 g. of diethyl malonate dissolved in a solution prepared by adding 1.8 g. of sodium to 100 ml. of absolute alcohol. When the reaction mixture was warmed, rapid evolution of trimethylamine occurred. The reaction mixture was held at 50° for twenty hours and then at 110° for another 21 hours. After removal of the alcohol, 100 ml. of dilute hydrochloric acid was added and the solution was extracted with ether. When the aqueous layer was made basic, an oil separated which was extracted with ether and dried over sodium sulfate. The ether was removed and the residue, on distillation, gave 9.5 g. (43%) of an orange-yellow oil; b.p. 184–185° at 0.3 mm., n_D^{20} 1.5419.

Anal. Calcd. for $C_{18}H_{21}NO_4$: C, 68.55; H, 6.71. Found: C, 68.62; H, 6.83.

The picrate of II was obtained from alcohol as yellow crystals, m.p. 93–94°.

Anal. Calcd. for $C_{24}H_{24}N_4O_{11}$: C, 52.94; H, 4.44. Found: C, 53.17; H, 4.65.

Ethyl β -(2-Quinoly)-ethylacetoacetate (III).—This was prepared in the same manner as described for II. From 20.0 g. of 2-(β -dimethylaminoethyl)-quinoline, using ethyl acetoacetate in fourfold excess, there resulted 12.5 g. (44%) of an orange-yellow oil; b.p. 185–196° at 0.4 mm., n_D^{20} 1.5620. The infrared absorption spectrum of III showed absorption peaks at 5.76 and 5.87 μ corresponding to the ester and ketone carbonyl groups, respectively. The picrate and styphnate of III formed as oils.

Anal. Calcd. for $C_{17}H_{19}NO_3$: C, 71.56; H, 6.71. Found: C, 71.79; H, 6.93.

1-(2'-Quinoly)-4-pentanone.—A solution of 7.8 g. of III was boiled under reflux for four hours with 30 ml. of 20% hydrochloric acid. The mixture was then neutralized with base and extracted with ether. After the ethereal solution had been dried over sodium sulfate, the ether was removed *in vacuo* and the residue was distilled to yield 3.2 g. (55%) of a yellow oil; b.p. 130–149° at 0.1 mm., n_D^{20} 1.5858. A sample of the oil, which was purified through the picrate for analysis, gave a value of n_D^{20} 1.5800. The infrared absorption spectrum of the purified oil showed an absorption peak at 5.87 μ but none at 5.76 μ .

Anal. Calcd. for $C_{14}H_{15}NO$: C, 78.84; H, 7.09. Found: C, 79.00; H, 7.29.

The picrate of 1-(2'-quinoly)-4-pentanone was obtained from alcohol as yellow crystals, m.p. 125–126°.

Anal. Calcd. for $C_{20}H_{18}N_4O_8$: C, 54.30; H, 4.10. Found: C, 54.60; H, 4.29.

Ethyl β -(2-Quinoly)-ethylbenzoylacetate (IV).—This was prepared in the same manner as II and III. From 20.0 g. of 2-(β -dimethylaminoethyl)-quinoline there was obtained 11.5 g. (33%) of a viscous orange oil; b.p. 180–200° at 0.01 mm., n_D^{20} 1.5920. Because of its high boiling point IV was difficult to purify and the analytical sample (n_D^{20} 1.5958) was obtained by repeated molecular distillation. The infrared absorption spectrum showed an ester carbonyl peak at 5.77 μ and a phenyl conjugated carbonyl peak at 5.96 μ . IV gave only oily picrates and styphnates.

Anal. Calcd. for $C_{29}H_{21}NO_3$: C, 76.05; H, 6.09. Found: C, 75.16; H, 6.49.

When 14.1 g. of IV was subjected to hydrolysis and decarboxylation by boiling with hydrochloric acid in the procedure described for the preparation of 1-(2'-quinoly)-4-pentanone, there was obtained 7.2 g. (64%) of a crude orange oil; b.p. 170–190° at 0.1 mm., n_D^{20} 1.6132. The infrared spectrum of the oil showed a peak at 5.97 μ (phenyl carbonyl) but none in the region of 5.70 to 5.80 μ . Treatment of the oil with picric acid in ethanol gave yellow crystals, m.p. 171–172°.

Anal. (picrate). Calcd. for $C_{25}H_{20}N_4O_8$: C, 59.52; H, 4.00. Found: C, 59.35; H, 4.12.

Reaction of VI with Diethyl Malonate.—This was carried out on a 0.1 molar scale using the same reaction conditions as for the preparation of II and using the same molar ratio of reactants. From the distillation of the reaction product two main fractions were taken and a fair amount of high-boiling material remained in the pot. Although the relative amounts of the two fractions varied in separate runs, the following is typical.

The lower boiling oil amounted to 4.5 g. of a pale yellow oil; b.p. 120–127° at 0.1 mm., n_D^{20} 1.6058. The infrared absorption spectrum of this oil showed an absorption peak at 11.07 μ which is in the region typical of terminal methylene absorption. This in conjunction with the composition of the material and its instability has led us to assign it structure VII.

Anal. Calcd. for $C_{14}H_{16}N_2$: C, 79.21; H, 7.60. Found: C, 79.21; H, 7.47.

The picrate of VII formed readily in ethanol as yellow crystals, m.p. 164–165°.

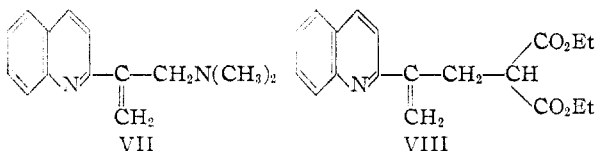
Anal. Calcd. for $C_{20}H_{19}N_6O_7$: C, 54.42; H, 4.34. Found: C, 54.30; H, 4.47.

The styphnate of VII was likewise obtained from ethanol as yellow crystals, m.p. 174–175° dec.

Anal. Calcd. for $C_{20}H_{19}N_6O_8$: C, 52.52; H, 4.09. Found: C, 52.44; H, 4.25.

The higher boiling oil amounted to 9.1 g. of a greenish-yellow oil; b.p. 160–180° at 0.04 mm., n_D^{20} 1.5558. The infrared absorption spectrum of the oil showed peaks at 5.76 and at 10.94 μ , as would be expected for an ester carbonyl and a terminal methylene group. Structure VIII is suggested for this oil.

Anal. Calcd. for $C_{15}H_{21}NO_4$: C, 69.70; H, 6.47. Found: C, 69.78; H, 6.75.



3-Carboethoxy-4-keto-5,6-benzoquinolizidine (V).—A mixture of 5.5 g. of II, 2.0 g. of Raney nickel catalyst and 20 ml. of absolute ethanol was subjected to hydrogenation at 100° under 150 atm. pressure of hydrogen. At the end of four hours, the hydrogen uptake roughly corresponded to two molar equivalents. After removal of the catalyst and solvent, the residual oil was distilled yielding 2.0 g. (42%) of a viscous oil; b.p. 188–190° at 0.2 mm., n_D^{20} 1.5551. The oil crystallized on prolonged standing and gave white crystals, m.p. 99–101°, from a benzene-hexane mixture.

Anal. Calcd. for $C_{16}H_{19}NO_3$: C, 70.30; H, 7.01. Found: C, 70.22; H, 7.22.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ROCHESTER
ROCHESTER, NEW YORK

RECEIVED MARCH 2, 1951

Fluorocarbon Chemistry. IV. The Preparation and Some Reactions of Silver Undecafluorocyclohexanecarboxylate

BY THOMAS J. BRICE^{1a} AND J. H. SIMONS^{1b}

The preparation of fluorocarbon derivatives, including carboxylic acids, by the electrochemical

(1) (a) Central Research Department, Minnesota Mining & Manufacturing Company, St. Paul 1, Minnesota. (b) Department of Chemical Engineering, University of Florida, Gainesville, Florida.

process² 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 laboratories⁴ and is similar to those reported by Henne and Finnegan⁵ 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. $60-70^\circ$. There was isolated 4.5 g. (54%) of $C_6F_{11}Br$, b.p. $90-92^\circ$ at ca. 735 mm., n_D^{20} 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. $109-112^\circ$ (736 mm.), n_D^{20} 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

(2) J. H. Simons, *et al.*, *J. Electrochem. Soc.*, **95**, 47 (1949).

(3) E. A. Kauck and A. R. Diesslin, 116th A.C.S. Meeting, Atlantic City, N. J., September, 1949.

(4) J. H. Simons and T. J. Brice, U. S. Patent 2,554,219, May 22, 1951.

(5) A. L. Henne and W. G. Finnegan, *THIS JOURNAL*, **79**, 3806 (1950).

(6) R. N. Haszeldine, *Nature*, **166**, 192 (1950).

Central Research Department of Minnesota Mining & Manufacturing Company for supplying the undecafluorocyclohexanecarboxylic acid used in these experiments.

FLUORINE LABORATORIES
THE PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENNA.

RECEIVED MARCH 17, 1951

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. $51-52^\circ$ (728 mm.); n_D^{20} 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_D^{20} 1.338-1.339. The

(1) (a) Central Research Department, Minnesota Mining & Manufacturing Company, St. Paul 1, Minnesota. (b) Department of Chemical Engineering, University of Florida, Gainesville, Florida.

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