alkali-resistant flask[8] and 2 g. of potassium hydroxide dissolved in 3 ml. of ethanol was added. Hydrolysis of the nitrile was carried out by refluxing for 48 hr. The mixture was acidified with 2*N* hydrochloric acid and washed with water. After being dried, VI was recrystallized from methanol. The yield was 730 mg. (82%), m.p. 127°. In order to increase the recovery of dihydroxystearic acid, the mother liquors were reextracted with 3 g. of unlabeled dihydroxystearic acid. The total recovery of radioactivity was 3.552 mc. (88.8%).

Ethyl 9,10-dibromostearate-1-C^{14} (VII). Enough inactive dihydroxystearic acid was added to VI to make a total of 5 g. Conversion to the dibromo-compound was carried out according to Ames and Bowman[4] with the use of hydrogen bromide-acetic acid and sulfuric acid. The yield of the crude dibromide ester was 6.5 g. (88.6%). The product was esterified by refluxing in a device diagrammed in Fig. 1 with 4 ml. of absolute alcohol, 10 ml. of benzene, and 0.17 ml. of concentrated sulfuric acid, water being removed azeotropically. The ester VII was run over a short column of activated alumina which retained most of the impurities. A sample had a b.p. of 235° at 1 mm.; bromine content calculated for $C_{20}H_{38}O_2Br_2$: Br, 34%. Found: 34.5%. The ester was a pale yellow oil. The yield was 5.1 g. (85%). It was used for the preparation of oleic-1-C^{14} acid without further purification.

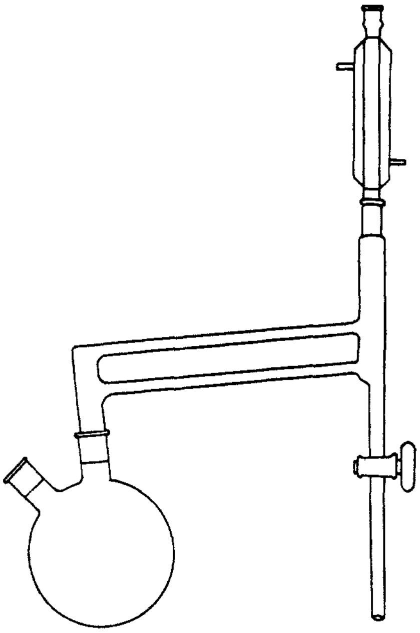

Figure 1

Oleic-1-C^{14} acid (VIII). Of zinc, 3 g. were activated by being boiled 5 min. with 15 ml. of ethanol and 1 ml. of 60% aqueous hydrobromic acid. The ethyl ester of VII was added to the zinc and the mixture refluxed under nitrogen for 2 hr. The zinc was removed by filtration and extracted with 1 g. of carrier ethyl oleate in petroleum ether for a more complete recovery of radioactive material. The combined filtrates were washed with 5% sulfuric acid and water and the solution was dried. Product VIII can be saponified directly without distillation. Saponification of the ethyl oleate was carried out with sodium ethoxide in absolute alcohol, followed by acidification with 2*N* hydrochloric acid. The yield of oleic-1-C^{14} acid was 3.7 g., m.p. 12°; iodine number calculated, 89.9. Found: 91.6. Radioactivity was determined by counting an infinitely thick sample after diluting with cold oleic acid in a gas-flow chamber.[9] The total activity was 2.4 mc. (60%) based on C^{14}-cyanide. The specific activity of the final product was 0.65 μc. per mg.

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[8] Corning "Boron Free."

[9] RCL Nucleometer, Scaler Type, Mark 9, Model 4.

Derivatives of Piperazine. XXXI. Salts of Piperazine and *N*-Phenylpiperazine for Utilization in Identification of Perfluoro-Organic Acids

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In research work involving the syntheses of fluorine organic compounds, the rapid identification of perfluoro-organic acids presented a problem as suitable derivatives have not been reported. Pollard *et al.*[1–5] have found the piperazine and *N*-phenylpiperazine salts of organic acids to be easily prepared and useful for identification. Haszeldine[6] reported the preparation of the piperazinium salt of perfluorobutyric acid.

It has been found that piperazine and *N*-phenylpiperazine react readily with perfluoro acids to form stable crystalline salts which can be readily purified. The monocarboxylic acids form piperazinium salts having a molecular ratio of 2 acid to 1 base. The dicarboxylic acid combines in a 1 to 1 molecular ratio. It is to be noted that the piperazinium salts of the 3, 4, 6, and 8 carbon acids melt within about 2° of each other. Mixed melting points of various combinations of these salts (approximately 50–50) show depressions of about 6°. The *N*-phenylpiperazinium salts of the 3 carbon acid and Kel F 8114 melt within 3° of each other. A mixture of these two salts (approximately 50–50) shows a depression of about 30°. The *N*-phenylpiperazinium salts of the 4, 6, and 8 carbon acids melt close together. Mixtures of various combinations of these salts (approximately 50–50) show depressions of from 15 to 20°. The mixed melting points were determined in sealed tubes.

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[1] C. B. Pollard and D. E. Adelson, *J. Am. Chem. Soc.*, **56**, 150 (1934).

[2] C. B. Pollard, D. E. Adelson, and J. P. Bain, *J. Am. Chem. Soc.*, **56**, 1759 (1934).

[3] C. B. Pollard and D. E. Adelson, *J. Am. Chem. Soc.*, **58**, 532 (1936).

[4] M. Prigot and C. B. Pollard, *J. Am. Chem. Soc.*, **70**, 2758 (1948).

[5] C. B. Pollard and N. S. Gidwani, *J. Org. Chem.*, **22**, 992 (1957).

[6] R. N. Haszeldine, *J. Chem. Soc.*, 2789 (1950).

TABLE I

PIPERAZINIUM SALTS OF PERHALO-ORGANIC ACIDS

		Data Concerning Piperazinium Salts								
			Calcd.				Found			
Fluoro Acid	Formula	M.P. °C.	C	H	F	Cl	C	H	F	Cl
Perfluoroacetic	CF_3COOH	229–231	30.6	3.85	36.3	...	30.08	3.79	36.64	...
Perfluoropropionic	CF_3CF_2COOH	241–242.5	29.0	2.92	45.9	...	29.54	3.11	45.58	...
Perfluorobutyric	$CF_3(CF_2)_2COOH$	240.8–241.8	28.0	2.35	51.8	...	28.25	2.52	51.64	...
Perfluorohexanoic	$CF_3(CF_2)_4COOH$	240.5–241.5	26.9	1.69	58.6	...	26.63	1.76	58.41	...
Perfluorooctanoic	$CF_3(CF_2)_6COOH$	240–241	26.3	1.54	62.36	...	26.48	1.41	62.19	...
Kel F 683	$Cl(CF_2\text{-}CFCl)_2CF_2COOH$	Above 250	23.64	1.49	...	26.16	23.85	1.65	...	26.42
Kel F 8114	$Cl(CF_2\text{-}CFCl)_3CF_2COOH$	Above 250	22.96	1.16	...	27.11	22.81	1.49	...	27.05
Perfluoroglutaric	$HOOC(CF_2)_3COOH$	269–270	33.15	3.71	34.96	...	33.24	3.62	34.68	...
Perfluoromethoxyacetic[a]	CF_3OCF_2COOH	191–191.5	26.9	2.76	42.6	...	27.11	2.70	42.83	...

[a] The preparation and structure determination of this acid will be the subject of a forthcoming publication.

TABLE II

N-PHENYLPIPERAZINIUM SALTS OF PERHALO-ORGANIC ACIDS

		Data Concerning N-Phenylpiperazinium Salts								
			Calcd.				Found			
Fluoro acid	Formula	M.P. °C.	C	H	F	Cl	C	H	F	Cl
Perfluoroacetic	CF_3COOH	151–154	52.2	5.48	20.6	...	52.32	5.48	20.82	...
Perfluoropropionic	CF_3CF_2COOH	144–144.5	47.8	4.64	29.1	...	47.72	4.52	29.38	...
Perfluorobutyric	$CF_3(CF_2)_2COOH$	124–126	44.7	4.02	35.4	...	44.33	4.00	35.61	...
Perfluorohexanoic	$CF_3(CF_2)_4COOH$	122–124	40.3	3.18	44.0	...	40.05	3.40	43.75	...
Perfluorooctanoic	$CF_3(CF_2)_6COOH$	125.5–128	37.5	2.62	49.5	...	37.63	2.62	50.10	...
Kel F 683	$Cl(CF_2\text{-}CFCl)_2CF_2COOH$	133–134	36.6	2.88	...	20.2	36.76	3.00	...	20.1
Kel F 8114	$Cl(CF_2\text{-}CFCl)_3CF_2COOH$	141–142	33.7	2.36	...	22.1	33.55	2.71	...	21.88

The melting points and mixed melting points of the piperazinium and *N*-phenylpiperazinium salts, in conjunction with the physical constants of the acids, have been useful in these laboratories for the identification of perfluoro organic acids.

Various attempts to obtain specimens of the 5 and 7 perfluoro acids proved futile.

Data concerning the piperazinium and N-phenylpiperazinium salts of perfluoro acids prepared are shown in Tables I and II.

EXPERIMENTAL

Piperazinium salts. About 1 ml. of the acid and 10 ml. of propanol-2 were placed in a small beaker packed in ice. Anhydrous piperazine was slowly added with stirring until the mixture was basic to litmus paper. Another 10 ml. portion of propanol-2 was added with stirring and the slurry was filtered while cold. Ten milliliters of boiling 95% ethanol were added to the crude product; water was added dropwise to the boiling mixture until the solid dissolved. The solution was cooled in an ice bath until crystallization was complete. Three recrystallizations gave a constant melting product.

The piperazinium salts of Kel F 683, Kel F 8114 and perfluoroglutaric acids were recrystallized from boiling water.

The piperazinium salt of perfluorooctanoic acid was crystallized from boiling 1-butanol.

N-Phenylpiperazinium salts. About 4 ml. of the acid and 20 ml. of propanol-2 were placed in a small beaker packed in ice. *N*-Phenylpiperazine was slowly added with stirring until the mixture was basic to litmus paper. The mixture was heated until the solid dissolved. The crystals which formed on cooling were recrystallized three times to give a constant melting product.

The *N*-phenylpiperazinium salts of Kel F 683 and Kel F 8114 acids were recrystallized from hot absolute ethanol.

The melting points were determined in sealed tubes by means of a brass block preheated to within 5 degrees of the respective melting point.

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Instability of Certain Organophosphorus Compounds Containing Pentavalent Phosphorus[1]

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In connection with the preparation of a variety of potentially toxic organophosphorus compounds,

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(2) Member of the Armed Forces assigned to the Army Chemical Corps.