Table I. Telomerization of Tetrafluoroethylene

run	reagent	tetrafluoroethylene (mol/mol reagent)	yield, %[a]	product composition, %		
				$I(CF_2)_2I$	$I(CF_2)_4I$	higher telomers
1	I_2	2	49.0	64.2	28.5	7.1
2	I_2	4	47.0	65.5	29.5	4.9
3	$I(CF_2)_2I$	1	50.3	66.6	29.1	4.1
4	$I(CF_2)_2I$	2	52.0	50.0	33.3	16.6
5	$I(CF_2)_2I$	4	67.0	34.1	41.4	24.3

[a] Includes recovered ICF_2CF_2I.

observed in all of the runs, suggesting an equilibrium dissociation of 1,2-diiodotetrafluoroethane to iodine and tetrafluoroethylene. This equilibrium is consistent with Haszeldine's proposed mechanism for telomer growth involving homolysis of iodo end groups.[2]

$$ICF_2CF_2I \rightleftharpoons ICF_2CF_2\cdot + I\cdot \rightleftharpoons CF_2{=}CF_2 + 2I\cdot$$

As one would expect, the results of the exploratory experiments indicate that higher ratios of tetrafluoroethylene to iodine favor conversion to higher telomers. For preparative work, the amount of tetrafluoroethylene that can be used is limited by the pressure capability of the equipment. Therefore, cylinders containing preparative reaction mixtures were cooled after 1 day of heating at 200–220 °C, recharged with tetrafluoroethylene, and heated for an additional day. In this way a 1-L pressure cylinder yielded 24 g of 1,4-diiodoperfluorobutane, 16 g of 1,6-diiodoperfluorohexane, 10 g of 1,8-diiodoperfluorooctane, and 10 g of a mixture of higher telomers.

Another method of obtaining higher telomers is to treat the lower homologues with tetrafluoroethylene. Treatment of 1,4-diiodoperfluorobutane with excess tetrafluoroethylene by this procedure resulted in 80% conversion to higher homologues, based on consumed starting material.

The fluorine NMR spectra of the α,ω-diiodoperfluoroalkanes are characteristic of the structure. The CF_2I signals all appear at ϕ 65, with the exception of ICF_2CF_2I (ϕ 59.6). The CF_2CF_2I signals appear at ϕ 114.4–115 and the internal CF_2 signals at ϕ 122.4–123.2.

Experimental Section

A Varian 920 chromatograph with a 10 ft × $^3/_8$ in. column of 10% QF-1 on acid-washed Chromosorb W was used for both analytical and preparative gas chromatography. NMR spectra were obtained with a Varian T-60 spectrometer. Pressure reactions were carried out behind a safety barricade by using 1800-psi-rated stainless-steel cylinders. Tetrafluoroethylene was purchased from PCR Inc.

Reaction of Tetrafluoroethylene with Iodine. Tetrafluoroethylene (50 mL, 0.84 mol) was condensed at −100 °C (ether–liquid nitrogen bath) into a previously evacuated calibrated glass trap fitted with a monometer. The tetrafluoroethylene was distilled into an evacuated 1000-mL stainless-steel pressure cylinder containing 63.5 g (0.25 mol) of iodine at −100 °C. The cylinder was heated behind a barricade with a 200–220 °C oil bath for 22 h. The cylinder was cooled, was recharged with 45 mL (0.75 mol) of tetrafluoroethylene by the above procedure, and was heated for an additional 18 h at 200–220 °C. The product was extracted with four 100-mL portions of methylene chloride, and the solution was washed with two 100-mL portions of 0.1 N sodium thiosulfate and dried over magnesium sulfate. Distillation gave 20.1 g (22.7%) of 1,2-diiodotetrafluoroethane [bp 42–47 °C (35 mm); ^{19}F NMR ($CDCl_3$) ϕ 59.6 (s)], 23.8 g (20.9%) of 1,4-diiodoperfluorobutane [bp 60–63 °C (35 mm); ^{19}F NMR ($CDCl_3$) ϕ 65.0 (t, 4 F, J = 0.2 Hz, CF_2I), 114.4 (t, 4 F, J = 0.2 Hz, CF_2)], 15.6 g (11.2%) of 1,6-diiodoperfluorohexane [bp 80–83 °C (15 mm); ^{19}F NMR ($CDCl_3$) ϕ 65.0 (t, 4 F, J = 0.2 Hz, CF_2I), 115.0 (m, 4 F, CF_2CF_2I), 122.4 (m, 4 F, CF_2)], and 10.5 g (6.4%) of 1,8-diiodoperfluorooctane [bp 95–98 °C (0.4 mm); mp 69–71 °C; ^{19}F NMR ($CDCl_3$) ϕ 65.0 (t, 4 F, J = 0.2 Hz, CF_2I), 115.0 (m, 4 F, CF_2CF_2I), 123.2 (m, 8 F, CF_2)]. The distillation residue contained higher telomers, including 1,10-diiodoperfluorodecane (3.9% yield by VPC) and 1,12-diiodoperfluorodecane (1.1% yield by VPC), and analytical samples were isolated by VPC: ^{19}F NMR ($CDCl_3$) ϕ 65.0 (m, 4 F, CF_2I), 115.0 (m, 4 F, CF_2CF_2I), 123.2 (m, 12 F and 16 F, respectively, CF_2).

Anal. Calcd for $C_4F_8I_2$: C, 10.59; F, 33.49; I, 55.93. Found: C, 10.76; F, 33.33; I, 55.88. Calcd for $C_6H_{12}I_2$: C, 13.01; F, 41.46; I, 45.83. Found: C, 12.84; F, 41.28; I, 45.83. Calcd for $C_8F_{16}I_2$: C, 14.70; F, 46.49; I, 38.82. Found: C, 14.65; F, 46.67; I, 38.76. Calcd for $C_{10}F_{20}I_2$: C, 15.93; F, 50.40; I, 33.67. Found: C, 15.94; F, 50.62; I, 33.47. Calcd for $C_{12}F_{24}I_2$: C, 16.88; F, 53.40; I, 29.72. Found: C, 16.80; F, 53.65; I, 29.46.

Reaction of 1,4-Diiodoperfluorobutane with Tetrafluoroethylene. A 150-mL stainless-steel cylinder charged with 45.4 g (0.10 mol) of 1,4-diiodoperfluorobutane and 6.5 mL (0.10 mol) of tetrafluoroethylene, by the above procedure, was heated for 28 h at 200–220 °C. Isolation of the products by the above procedure gave 14.2 g (31.2%) of recovered 1,4-diiodoperfluorobutane, 17.5 g (45% based on consumed starting material) of 1,4-diiodoperfluorohexane, and 14.2 g of a crude mixture of higher telomers.

Registry No. $I(CF_2)_2I$, 354-65-4; $I(CF_2)_4I$, 375-50-8; $I(CF_2)_6I$, 375-80-4; $I(CF_2)_8I$, 335-70-6; $I(CF_2)_{10}I$, 65975-18-0; $I(CF_2)_{12}I$, 72049-11-7; $CF_2{=}CF_2$, 116-14-3; I_2, 7553-56-2.

Synthesis of 2-Fluoro-7,12-dimethylbenz[*a*]anthracene[1]

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The reasons for synthesizing fluorinated derivatives of 7-methylbenz[*a*]anthracene, **1**, and 7,12-dimethylbenz[*a*]anthracene, **2**, have been stated.[3] In continuation of this effort to understand the detoxification and carcinogenic metabolic pathways of **1** and **2**, we report the synthesis of 2-fluoro-7,12-dimethylbenz[*a*]anthracene, **3**, by the reactions outlined in Scheme I.

Reaction of phthalic anhydride with the Grignard reagent prepared from 1-bromo-7-fluoronaphthalene[4] afforded *o*-(7-fluoro-1-naphthoyl)benzoic acid, **4**, in 91% yield only when sublimed magnesium and ethylene dibromide[5] were used in the preparation of the Grignard reagent. The remaining steps from **4** to **3** all went in excellent yields as shown in Scheme I.

The carcinogenic activity of **3** has been tested by Drs. James A. and Elizabeth C. Miller, McArdle Laboratory for Cancer Research, University of Wisconsin, who found that

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(2) Postdoctoral Research Associate.

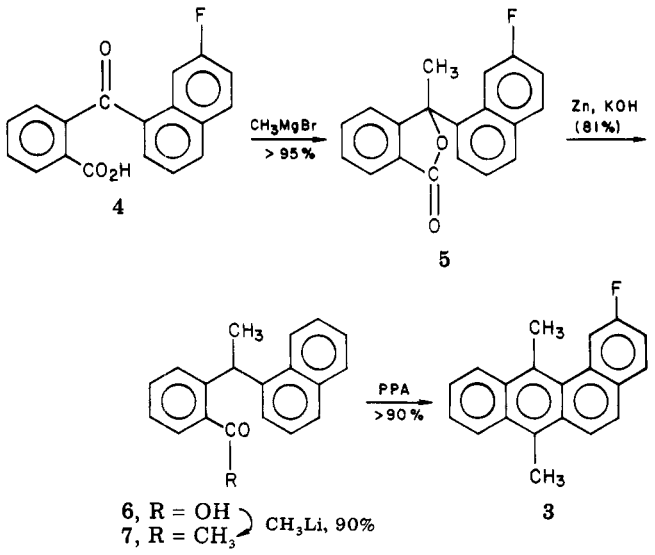
(3) Newman, M. S.; MacDowell, D.; Swaminathan, S. *J. Org. Chem.* **1959**, *24*, 509.

(4) Adcock, W.; Dewar, M. J. S. *J. Am. Chem. Soc.* **1967**, *89*, 386.

(5) Pearson, D. W.; Cowan, D.; Beckler, J. D. *J. Org. Chem.* **1959**, *24*, 504.

0022-3263/80/1945-0348$01.00/0

Scheme I



no tumors has appeared in 18 male Fischer rats 20 months after injection.

Randomly tritiated[6] **3** showed decreased bonding to DNA in cell culture[7] which fact correlates with the findings of the Millers (above).

The fact that **3** was noncarcinogenic lends support to the bay region diol epoxide hypothesis in the benz[*a*]anthracene series[8] because the presence of a fluorine atom in the 2-position would be expected to prevent such metabolism, as is the case.

Experimental Section[9]

γ-(*p*-Fluorophenyl)butyric Acid. This was prepared in 75% overall yield by condensation of fluorobenzene with succinic anhydride followed by Clemmensen reduction as described.[10]

1-Amino-7-fluoronaphthalene. Ring closure of the above acid via its acid chloride gave 7-fluoro-3,4-dihydro-1(2*H*)-naphthalenone, bp 120–121 °C (2 mm), in 88% yield. This ketone was converted to the oxime and the latter to 7-fluoro-1-naphthylamine, bp 140–145 °C (3 mm), as described for other similar conversions.[11] This amine was converted to 1-bromo-7-fluoronaphthalene, bp 125–127 °C (3 mm), mp 42–43 °C, in 45% yield.[12]

***o*-(7-Fluoro-1-naphthoyl)benzoic Acid*, 4.** A solution of 13.6 g (60 mmol) of 1-bromo-7-fluoronaphthalene[4] in 100 mL of ether (distilled from butylmagnesium bromide solution), 50 mL of dry benzene, and 0.5 mL of ethylene dibromide[5] was added during 1 h to a stirred mixture of 4 g (167 mmol) of pure sublimed magnesium in 25 mL of ether. After 0.5 h at reflux the clear pale yellow solution was transferred under N_2 to an addition funnel and added rapidly to a stirred hot solution of 9.6 g (65 mmol) of phthalic anhydride in 250 mL of benzene. After being held at reflux for 5 h, the acidic product was isolated to yield 16.1 g (91%) of **4**, mp 206–208 °C, suitable for the next step. The analytical sample was obtained with little loss by recrystallization from benzene to yield pure colorless **4**, mp 212–213 °C.

3-(7-Fluoro-1-naphthyl)-3-methylphthalide*, 5. A solution of 12.5 g (42 mmol) of **4** in 400 mL of dry ether and 100 mL of dry benzene was added to 50 mL of 2.7 M methylmagnesium bromide (Ventron), and the mixture was refluxed for 1 h. From the neutral fraction of the reaction mixture was obtained 12.0 g (96%) of yellowish solid, **5**, mp 140–143 °C (IR band at 5.7 μm), pure enough for the next step. Recrystallization from benzene–petroleum ether afforded the analytical sample, mp 152–154 °C, with little loss.

2-[α-(7-Fluoro-1-naphthyl)ethyl]benzoic Acid*, 6. A stirred mixture of 11.5 g (39 mmol) of **5**, 70 g of zinc dust (activated by brief treatment with $CuSO_4$), 520 mL of 10% KOH, and 65 mL of pyridine was held at reflux for 26 h. From the acid fraction was obtained 9.3 g (81%) of **6**, mp 153–155 °C, good enough for the next step. The colorless analytical sample, mp 155.0–156.5 °C, was obtained by crystallization from aqueous alcohol with little loss.

2-[α-(7-Fluoro-1-naphthyl)ethyl]acetophenone*, 7. To a solution of 9.5 g (32 mmol) of **6** in 650 mL of dry ether was added slowly 50 mL of 1.8 M CH_3Li (Ventron), and the mixture was refluxed for 2 h. From the neutral fraction of the reactants was isolated 8.8 g (93%) of **7**, mp 116–118 °C, and a small amount of **6** was recovered from the acidic fraction. Recrystallization from benzene–petroleum ether yields pure **7**, mp 122–123 °C, with little loss.

3-Fluoro-7,12-dimethylbenz[*a*]anthracene*, 3. To warm (45 °C) stirred polyphosphoric acid (115%) was added 8.4 g (29 mmol) of **7**. The mixture was heated to 90–95 °C, kept there for 30 min, cooled, and poured on ice. The product was taken into ether–benzene and isolated to yield 7.7 g (98%) of **3**, mp 86–89 °C. The crude mixture was treated with 6.6 g of picric acid in benzene and the crystalline picrate recrystallized to a constant melting point of 130–131 °C. This picrate was then treated with an aqueous solution of diethanolamine to remove the picric acid. Recrystallization of the resulting **3** from benzene–ethanol afforded 4.5 g (57%) of **3**, mp 96.5–97.5 °C. Chromatography over alumina and recrystallization yielded (with little loss) the purest **3**, mp 97.5–98.5 °C, for testing purposes.

Registry No. **3**, 68141-56-0; **3** picrate, 72017-22-2; **4**, 71276-91-0; **5**, 72017-23-3; **6**, 72017-24-4; **7**, 72017-25-5; α-(*p*-fluorophenyl)butyric acid, 589-06-0; 1-amino-7-fluoronaphthalene, 13916-95-5; 7-fluoro-3,4-dihydro-1(2*H*)-naphthalenone, 2840-44-0; 1-bromo-7-fluoronaphthalene, 13790-91-5; phthalic anhydride, 85-44-9.

(6) A new synthesis of **3** has been used. See: Sheikh, Y. M.; Cazer, F. D.; Hart, R. W.; Witiak, D. T., submitted for publication in *J. Org. Chem.*

(7) See: Daniel, F. B.; Wong, L. K.; Oravec, C. T.; Cazer, S. D.; Wang, C.-L. A.; D'Ambrosio, S. M.; Hart, R. W.; Witiak, D. T. "Proceedings of the 3rd International Symposium on Polycyclic Aromatic Hydrocarbons"; Oct 25–27, 1978, in press.

(8) For a review of the development of concepts see: Heidelberger, C. In "Carcinogenesis"; Raven Press: New York, 1976; p 1 and references therein.

(9) All melting and boiling points are uncorrected and are in °C. All new compounds marked with an asterisk gave results within ±0.3% of the correct analytical results by Galbraith or MHW Laboratories. The usual way of working up a reaction mixture was to wash a benzene–ether solution of the products with alkali, to remove the acid portion, or acid. The solvents were then extracted with saturated NaCl solution and dried by passing them over $MgSO_4$.

(10) Newman, M. S.; Chatterji, R.; Seshadri, S. *J. Org. Chem.* **1961**, *26*, 2667.

(11) Newman, M. S.; Hung, W. M. *J. Org. Chem.* **1973**, *38*, 4073.

(12) Newman, M. S.; Wise, P. H. *J. Am. Chem. Soc.* **1941**, *63*, 2847. See also ref 4.

Kinetics of Acetylation of Substituted 4-Thianols. Single-Crystal Analysis of *cis*-2,*trans*-6-Diphenyl-*cis*-3-ethylthian-*r*-4-ol and 2,2,6,6-Tetramethyl-4(e)-phenylthian-4(a)-ol

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The synthesis[1] and ^{13}C NMR analyses[2] of a large number of highly substituted 1-hetera-2,6-diaryl-4-cyclohexanones

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