idative loss of the hydroxymethyl group in the bicyclo[3.3.1]nonanes studied by him.[3] In these molecules and in **5** oxidative loss of the hydroxymethyl group is probably due to facile enolization of an aldehyde intermediate. Enol formation in such bicyclo[3.3.1]nonane derivatives should be favored by relief of steric crowding between bridges. Enols have been implicated in the chromic acid cleavage of ketones.[8]

Although the generation of **4** represents an unusual PDC oxidation, the success of this reaction allows the preparation of the diketone in three convenient steps and in greater than 70% overall yield. Since **4** has been utilized in the synthesis of several heteroadamantanes,[2] the convenience of our preparative method may have general utility.

Experimental Section

General Methods. Melting points are uncorrected. NMR spectra were taken on a Varian CFT-20 or EM-360L spectrometer as $CDCl_3$ solutions, and chemical shifts are reported as downfield shifts (ppm) from tetramethylsilane. Infrared spectra were taken on a Beckman Accu Lab 4. High-resolution mass spectra were obtained on an AEI MS-9 double-focusing instrument.

2-Oxatricyclo[4.3.1.1^{4,8}]undecan-9-one (2). *m*-Chloroperbenzoic acid (3.94 g, ~20 mmol, Technical Grade, 85%) was added to a solution of 2-adamantanone (3.00 g, 20.0 mmol) in dichloromethane (50 mL), and the solution was stirred at ambient temperature overnight. The solution was filtered, washed with 100 mL of 1 N NaOH, dried over $MgSO_4$, and concentrated under reduced pressure to give 3.23 g (98%) of a white solid, mp 285–287 °C (lit.[4] mp 286–288 °C).

7-(Hydroxymethyl)bicyclo[3.3.1]nonan-3-ol (3). The diol was prepared by the addition of **2** (5.44 g, 32.7 mmol) in anhydrous ether to a suspension of lithium aluminum hydride (1.24 g, 32.7 mmol) in the same solvent. After the addition was complete, the solution was refluxed for 3 h, cooled, and quenched with 1.24 mL of water, 1.24 mL of 1 N NaOH, and 3.72 mL of water. The ether phase was separated, and the alumina salts were washed with hot tetrahydrofuran (THF). The ether and THF solutions were combined, dried over $MgSO_4$, and evaporated under reduced pressure to give 5.28 g (96%) of a white solid, mp 164–165 °C (lit.[5] mp 167–168 °C).

Bicyclo[3.3.1]nonane-3,7-dione (4). The diketone was prepared by the addition of **3** (3.00 g, 17.6 mmol) in one portion to a solution of pyridinium dichromate (66.3 g, 176 mmol) in CH_2Cl_2 (160 mL) at room temperature. The solution was stirred overnight,[9] diluted with diethyl ether, filtered through a short Florisil column, dried over $MgSO_4$, and concentrated under reduced pressure to give 2.03 g (75%) of diketone, mp 250 °C (lit.[2] mp 252 °C), with spectral properties identical with those of an authentic sample.[2] This reaction could also be conveniently carried out on 10 g of diol **3**, and on this scale too a 75% yield of diketone **4** was obtained.

7-(Hydroxymethyl)bicyclo[3.3.1]nonan-3-one (5). The diol **3** (0.500 g, 2.94 mmol) was added to a solution of pyridinium dichromate (5.08 g, 13.5 mmol) in 35 mL of CH_2Cl_2. After being stirred for 2 h, the solution was diluted with ether, filtered through a short Florisil column, dried over $MgSO_4$, and evaporated under reduced pressure to give 0.404 g of product. This material was purified by chromatography on a column of neutral alumina, which was eluted with a 60:40 mixture of ethyl acetate–chloroform, yielding 0.240 g (50%) of a mixture of hydroxy ketone **5** and lactol **6**; mp 88–92 °C. The ^1H NMR spectrum ($CDCl_3$) of the mixture showed δ 1.45 (br s, 2 H), 1.87 (m, 10 H), 2.30 (br s, ~1 H), 2.70 (s, 1 H, exchangeable in D_2O), 3.27 (d, 0.4 H, $J = 7$ Hz), and 3.75 (d, 1.6 H, $J = 3$ Hz). On addition of a crystal of oxalic acid to the solution to accelerate the interconversion of **5** and **6**, the resonance at δ 2.30, ascribed to the protons α to the carbonyl in **5**, moved upfield so that it became part of the broad singlet centered at δ 1.87. In addition, the doublets at δ 3.27 and 3.75, assigned to the protons of the hydroxymethyl group in, respectively, **5** and **6**, merged to a broad 2-H singlet at δ 3.67. The ^{13}C spectrum ($CDCl_3$) of the mixture of **5** and **6** showed δ 26.84, 28.31, 28.83, 30.94, 31.69, 33.64, 34.69, 36.17, 43.98, 50.07, 67.69, 71.17, and 100.84. No attempt was made to locate the very small resonance expected for the carbonyl carbon in **5**. The IR spectrum (CH_2Cl_2) showed an OH signal at 3400 cm^{-1} and a relatively weak C=O signal at 1725 cm^{-1}.

Exact mass calcd for $C_{10}H_{16}O_2$: m/e 168.1149. Found: m/e 168.1154.

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Registry No. **1**, 700-58-3; **2**, 21898-84-0; **3**, 66674-81-5; **4**, 770-15-0; **5**, 72036-39-6; **6**, 72036-40-9.

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[9] With some batches of PDC it proved necessary to reflux the reaction mixture overnight in order to complete the reaction. The results of the control experiments involving the oxidation of benzyl alcohol and cyclohexylmethanol were not affected by this change in reaction conditions.

Preparation of α,ω-Diiodoperfluoroalkanes[1]

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Although perfluoroalkyl iodides are widely used reagents for the synthesis of fluorinated compounds, α,ω-diiodoperfluoroalkanes have not been readily accessible. A direct route to these materials by the telomerization of tetrafluoroethylene with iodine was reported by Haszeldine in 1951, but experimental details and product characterizations were not given.[2] Subsequently, Knunyants et al. attempted to repeat this work but obtained only very low yields of a mixture of telomers.[3] Although catalysts for the reaction were reported in the patent literature,[4] this direct method has not appeared to be useful for laboratory-scale preparations, and other routes have been developed. A hot-tube reaction of diacid chlorides with potassium iodide has been reported to give α,ω-diiodoperfluoroalkanes, but the preparation of the starting materials required several steps.[5] Milligram quantities of several of the diiodides were obtained by the photolysis of bromoiododifluoromethane with tetrafluoroethylene.[6]

We wish to report the development of a convenient and reproducible laboratory-scale telomerization of tetrafluoroethylene with iodine. The results of exploratory experiments are summarized in Table I. The reactions were carried out in stainless-steel cylinders at 200–220 °C and an initial pressure of 20–27 atm. No catalysts were used.

Either iodine or 1,2-diiodotetrafluoroethane can be used interchangeably as the telogen as is seen by the similarity of the results of runs 1 and 3 of Table I, which contained equivalent amounts of starting materials. Free iodine was

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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.

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