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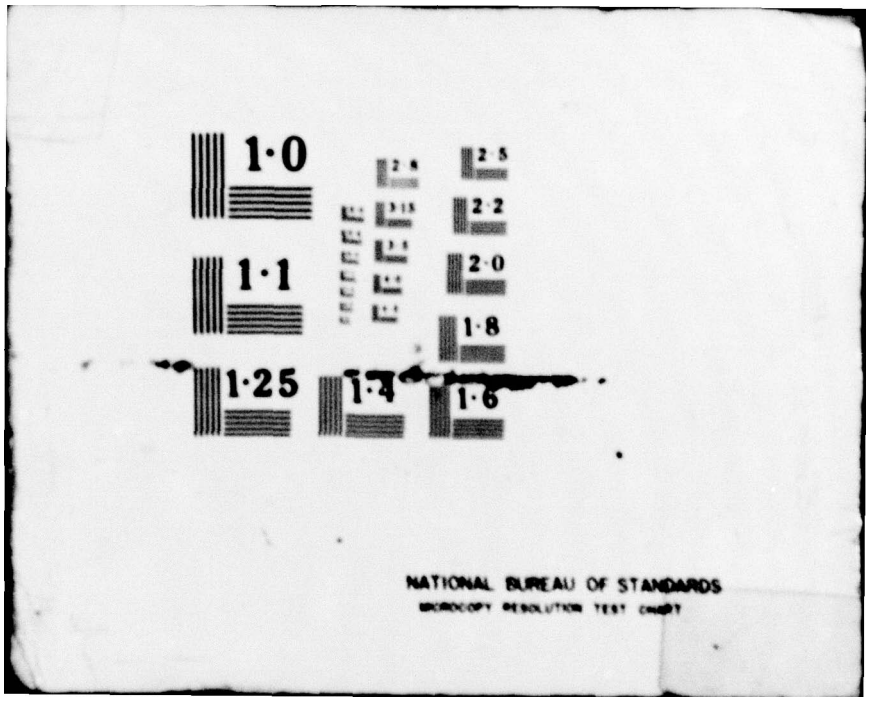
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Preparation of α,ω-Diiodoperfluoroalkanes

by

Clifford D. Bedford and Kurt Baum

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Fluorochem, Inc.
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Reaction conditions for the preparation of α,ω-diiodoperfluoroalkanes from iodine and tetrafluoroethylene were studied. A laboratory method was developed for the preparation of ~~multigram~~ quantities of α,ω-diiodoperfluoroalkanes. Similar results were observed using ~~iodine~~ and 1,2-diiodoperfluoroethane. A high conversion of 1,4-diiodoperfluorobutane to higher telomers was obtained.

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Preparation of α,ω-Diiodoperfluoroalkanes[1]

Clifford D. Bedford and Kurt Baum*

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Abstract

Reaction conditions for the preparation of α,ω-diiodoperfluoroalkanes from iodine and tetrafluoroethylene were studied. A laboratory method was developed for the preparation of multigram quantities of α,ω-diiodoperfluoroalkanes. Similar results were observed using iodine and 1,2-diiodoperfluoroethane. A high conversion of 1,4-diiodoperfluorobutane to higher telomers was obtained.

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.

Table I. Telomerization of Tetrafluoroethylene

Run	Reagent	Tetrafluoroethylene (moles/mole 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

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 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]

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

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 a day of heating at 200-220°C, recharged with tetrafluoroethylene and heated for an additional day. In this way a one liter 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 homologs with tetrafluoroethylene. Treatment of 1,4-diiodoperfluorobutane with excess tetrafluoroethylene by this procedure resulted in 80% conversion to higher homologs, 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 (59.6). The $\underline{CF_2}CF_2I$ signals appear at 114.4-115, and the internal CF_2 signals, at 122.4-123.2.

Experimental Section

A Varian 920 chromatograph with a 10 ft x 3/8 inch 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 using 1800 PSI rated stainless steel cylinders. Tetrafluoroethylene was purchased from PCR Inc.

Reaction of Tetrafluoroethylene with Iodine. Tetrafluoroethylene (50 ml, 0.84 mole) 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 mole) of iodine at -100°C. The cylinder was heated behind a barricade with a 200-220°C oil bath for 22 hrs. The cylinder was cooled, was recharged with 45 ml (0.75 mole) of tetrafluoroethylene by the above procedure, and was heated for an additional 18 hrs 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 ppm (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) and 114.4 ppm (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, $\underline{CF_2}CF_2I$) and 122.4 ppm (m, 4 F, CF_2); 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, $\underline{CF_2}CF_2I$) and 123.2 ppm (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, $\underline{CF_2}CF_2I$) and 123.2 ppm (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 mole) of 1,4-diiodoperfluorobutane and 6.5 ml (0.10 mole) of tetrafluoroethylene, by the above procedure, was heated for 28 hrs 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.

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(1) This work was supported by the Office of Naval Research.

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