[CONTRIBUTION FROM THE CHEMISTRY DIVISION, NAVAL RESEARCH LABORATORY]

Some New Polyfluoroalkyl Halides, $H(CF_2)_nCH_2X$, and the Reactions of $H(CF_2)_nCH_2I$ with Water, Sulfur and Selenium

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RECEIVED APRIL 2, 1956

Results are reported on the thermally induced reactions of $H(CF_2)_nCH_2I$, where n is 6 or 10, with water. sulfur and selenium. Reactions of $H(CF_2)_6CH_2I$ with water at 180–250° lead mainly to the formation of $H(CF_2)_6CH_3$ in yields ranging from 20 to 33%. At 250–270° the reaction of $H(CF_2)_6CH_2I$ with sulfur proceeds smoothly to give $H(CF_2)_6CH_2CH_2(CF_2)_6H$, $H(CF_2)_6CH_2SCH_2(CF_2)_6H$, $H(CF_2)_6CH_2SSCH_2(CF_2)_6H$ and I_2. Analogous compounds are produced by the reaction of either $H(CF_2)_6CH_2I$ or $H(CF_2)_{10}CH_2I$ with selenium. A free radical mechanism involving the homolytic cleavage of the C–I bond is postulated to explain the products of these reactions.

Introduction

This paper is concerned with reactions involved in the preparation of symmetrical ethers, sulfides and selenides, containing $H(CF_2CF_2)_nCH_2-$ substituents. Since no methods have been published for the preparation of these compounds, several routes for their synthesis were investigated. The telomeric fluoroalcohols, $H(CF_2CF_2)_nCH_2OH$,[1,2] were used as starting materials. To facilitate discussion, the abbreviations used in our earlier studies[3] are employed here. Thus, the $H(CF_2CF_2)_nCH_2-$ substituent is designated as a ψ'-alkyl group, *e.g.*, $H(CF_2CF_2)_3CH_2I$ is ψ'-heptyl iodide.

Results and Discussion

General Observations.—As intermediates several hitherto unreported ψ'-alkyl *p*-toluenesulfonates (tosylates) and ψ'-alkyl halides were prepared by methods[4–6] recently shown to be successful in the preparation of corresponding derivatives of the 1,1-dihydroperfluoroalcohols. The ψ'-heptyl tosylate (1H,1H,7H-dodecafluoroheptyl tosylate) and ψ'-undecyl tosylate (1H,1H,11H-eicosafluoroundecyl tosylate) were observed to be remarkably stable, both thermally and hydrolytically. ψ'-Heptyl tosylate distills at 290–300° with only slight decomposition and is hydrolyzed about 5% after being stirred 24 hours in a stoichiometric quantity of refluxing 10% sodium hydroxide. Hydrolysis proceeds more rapidly at 200–225° in stirred diethylene glycol mixtures containing suspended sodium hydroxide or sodium sulfide. At ordinary temperatures, the ψ'-heptyl halides (1H,1H,7H-dodecafluoroheptyl chloride, bromide and iodide) and the ψ'-undecyl iodide (1H,1H,11H-eicosafluoroundecyl iodide) are also stable thermally and hydrolytically. Identifying properties of the ψ'-alkyl tosylates and halides are summarized in Table I.[7–11]

Neither ψ'-heptyl tosylate nor ψ'-heptyl halides reacted with $H(CF_2)_6CH_2ONa$ (sodium 1H,1H,7H-dodecafluoroheptoxide) to give bis-(ψ'-heptyl) ether, *i.e.*, bis-(1H,1H,7H-dodecafluoroheptyl) ether. Under comparable conditions alkyl tosylates and phenyl halides afford practicable yields of dialkyl ethers[12] and diphenyl ether.[13] The reluctance of related 1,1-dihydroperfluoroalkyl halides to undergo certain familiar displacement reactions has been reported.[14] It is believed the desired bis-(ψ'-heptyl) ether may be prepared by Hanford's reaction[15] of tetrafluoroethylene with ψ'-heptyl methyl ether (1H,1H,7H-dodecafluoroheptyl methyl ether).[3]

Thermal Reactions of ψ'-Heptyl Iodide with Water.—Aqueous reactions of alkyl halides with sodium sulfite at 180° furnish alkane sulfonates in good yield.[16,17] Under comparable conditions ψ'-heptyl iodide reacts to give 33% ψ'-heptyl hydride (1H,1H,1H,7H-dodecafluoroheptane) and 5% ψ'-heptyl mercaptan (1H,1H,7H-dodecafluoroheptyl mercaptan), together with unidentified products of lower molecular weight. At higher temperatures (250°), ψ'-heptyl iodide reacts with aqueous sodium sulfide to give 18.7% yield ψ'-heptyl hydride as well as small amounts of bis-(ψ'-heptyl), *i.e.*, 1H,7H,7H,8H,8H,14H-tetraeicosafluorotetradecane, and bis-(ψ'-heptyl) sulfide, *i.e.*, bis-(1H,1H,7H-dodecafluoroheptyl) sulfide. These latter products stand in contrast with the 72% yield of diphenyl sulfide and 16% yield of thiophenol which result from the reaction of phenyl chloride with aqueous sodium sulfide.[18]

The main course of the reaction of ψ'-heptyl iodide with water at high temperatures is believed to be hydrogen abstraction similar to that observed with perfluoroalkyl halides.[19] This explanation is supported by the failure of ψ'-heptyl iodide to give ψ'-heptyl hydride after refluxing for 2 hours with 10% alcoholic potassium hydroxide. Under corresponding conditions with alcoholic potassium hydroxide, perfluoroalkyl iodides are reported to give perfluoroalkyl hydrides[20–22] by a "positive iodine" mechanism. Identity of ψ'-heptyl hydride has been confirmed by the reduction of ψ'-

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TABLE I

NEW COMPOUNDS CONTAINING $H(CF_2CF_2)_nCH_2-$ SUBSTITUENTS

Compound	B.p. °C.	B.p. Mm.	M.p., °C.	$n^{20}D$	d^{20}_4	AR_F[b] Atomic	AR_F[b] Bond	Formula	Analyses, %[a] Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Fluorine Calcd.	Fluorine Found	Other Calcd.	Other Found
$H(CF_2)_6CH_2OSO_2C_6H_4CH_3$	126	0.5	*ca.* 33	1.4123[c]	1.592[c]	1.19		$C_{14}H_{10}F_{12}SO_3$	34.57	32.7[d]	2.07	2.09	46.89	45.2[d]	6.60	6.65
$H(CF_2)_{10}CH_2OSO_2C_6H_4CH_3$	149	0.5	77–80					$C_{18}H_{10}F_{20}SO_3$							4.67	4.49
$H(CF_2)_6CH_2Cl$	141–143	760		1.3189	1.7051	1.132	1.778	$C_7H_3F_{12}Cl$							10.12	9.99
$H(CF_2)_6CH_2Br$	157–159	760		1.3350	1.887	1.11	1.76	$C_7H_3F_{12}Br$							20.23	20.4
$H(CF_2)_6CH_2I$	78–79	20.0		1.3643	2.0441	1.088	1.735	$C_7H_3F_{12}I$	19.02	19.2	0.68	0.64	51.58	52.0	28.71	28.6
$H(CF_2)_{10}CH_2I$	190	200	82–85					$C_{11}H_3F_{20}I$	20.58	20.7	0.47	0.61	59.19	59.5	19.77	20.0
$H(CF_2)_6CH_2SH$	70–71	20.0		1.3378	1.6700	1.122	1.769	$C_7H_4F_{12}S$	24.15	24.16	1.16	1.15			9.21	9.22
$H(CF_2)_6CH_3$[e]	108–110	760		1.298	1.608	1.18	1.97	$C_7H_4F_{12}$	26.60	26.7	1.27	1.27	71.13	71.9		
$H(CF_2)_6CH_2CH_2(CF_2)_6H$	135	20.0	33–34	1.3104[f]				$C_{14}H_6F_{24}$	26.68	26.8	0.96	0.97	72.36	72.4		
$H(CF_2)_6CH_2SCH_2(CF_2)_6H$	159–160	20.0		1.3370	1.7822	1.121	1.768	$C_{14}H_6F_{24}S$	25.39	25.5	0.91	0.95			4.84	4.76
$H(CF_2)_6CH_2SeCH_2(CF_2)_6H$	150	10.0		1.3468	1.8892	1.127		$C_{14}H_6F_{24}Se$	23.71	23.8	0.85	0.82	64.30	64.5	11.13	11.0
$H(CF_2)_6CH_2SeSeCH_2(CF_2)_6H$	170–175	10.0		1.378	1.979	1.126		$C_{14}H_6F_{24}Se_2$							20.04	20.2
$H(CF_2)_{10}CH_2SeCH_2(CF_2)_{10}H$	170	0.6	94–96[g]					$C_{22}H_6F_{40}Se$	23.82	23.8	0.54	0.59	68.52	68.0	7.12	6.98

[a] All elemental assays were performed by the Schwarzkopf Microanalytical Laboratory. [b] The atomic refraction of fluorine, AR_F, was calculated by subtracting the required atomic[7] or bond[8] increments by Vogel from the Lorentz–Lorenz molecular refraction. For the $-OSO_2-$ group refractivity, the mean value of 10.5[9] was used. The value 10.61[10] was used for Se in monoselenides and the value 11.17[11] for Se in diselenides. [c] Measurements made on supercooled liquid. [d] The combination of elements here made analysis difficult. [e] Infrared spectra indicate trace impurities. [f] Measurement was made at 37.5°. [g] After recrystallization from chloroform.

heptyl iodide with lithium aluminum hydride. The mechanism and stoichiometry of this reduction have not been investigated, but it is evident that ψ'-heptyl iodide is unusually resistant to reduction.

Thermal Reaction of ψ'-Heptyl Iodide with Sulfur.—Although conditions for optimum yields have not been determined, this reaction proceeds smoothly at 250–270°, with good material balance, to give bis-(ψ'-heptyl), bis-(ψ'-heptyl) sulfide, bis-(ψ'-heptyl) disulfide, traces of bis-(ψ'-heptyl) polysulfides and iodine. Properties of the monosulfide and ψ'-heptyl mercaptan, obtained by the reduction of bis-(ψ'-heptyl) disulfide, are given in Table I. The mechanism by which the thermal reaction proceeds is believed to involve the homolysis of ψ'-heptyl iodide to $H(CF_2)_6CH_2\cdot$ radicals and atomic iodine. The homolytic cleavage of the C–I bond in perfluoromethyl iodide and perfluoropropyl iodide has been postulated to explain the formation of corresponding perfluoroalkyl analogs of sulfur.[23–26] Since perfluoroethane and perfluorohexane were not observed in the latter reactions, it is of interest that bis-(ψ'-heptyl) was found in our reaction. This new dimeric derivative is believed to result from the reaction of two ψ'-heptyl radicals. Identity of bis-(ψ'-heptyl) was confirmed by independent synthesis.[27] Heretofore, Henne's coupling reaction has been applied successfully only to certain fluoro compounds with the terminal $-CF_2X$ or $-CFClX$, where X is bromine or iodine.[27]

Bis-(ψ'-heptyl) disulfide is reduced normally to ψ'-heptyl mercaptan, which in turn forms mercaptides and otherwise shows the expected functional behavior of a mercaptan. In contrast, perfluoromethanethiol, CF_3SH, is not a true mercaptan; it decomposes into ionic fragments on treatment with aqueous sodium hydroxide.[26]

Thermal Reactions of ψ'-Alkyl Iodides with Selenium.—These reactions proceed to give products analogous with those obtained in the reaction of ψ'-heptyl iodide with sulfur. The expected reactions of free ψ'-alkyl radicals satisfactorily explain the products obtained. Bis-(ψ'-heptyl) selenide, *i.e.*, bis-(1H,1H,7H-dodecafluoroheptyl)selenide and bis-(ψ'-undecyl) selenide, *i.e.*, bis-(1H,1H,11H-eicosafluoroundecyl) selenide, are resistant to heat and to alkaline hydrolysis. The corresponding bis-(ψ'-alkyl) diselenides differ in reactions from the reported bistrifluoromethyl diselenide, $CF_3SeSeCF_3$.[28] Reduction of bis-(ψ'-alkyl) diselen-

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ides occurs normally with lithium aluminum hydride in ether. The ψ'-heptyl selenomercaptan (1H,1H,7H-dodecafluoroheptyl selenomercaptan) is readily oxidized by the air to the bis-(ψ'-heptyl) diselenide. The distillation of this air-oxidized material affords a convenient route to the pure bis-(ψ'-heptyl) diselenide. With respect to oxidation, the ψ'-alkyl selenomercaptans resemble the better known alkyl selenomercaptans. As expected, the ψ'-heptyl selenomercaptan is substantially more sensitive to atmospheric oxidation than is the corresponding mercaptan.

Analogous Reactions of Other Fluoroalcohols.—Analogous reactions of the iodides of other highly fluorinated aliphatic alcohols are under study and will be reported later.

Experimental

Apparatus and Procedure.—All thermal reactions were carried out at autogenous pressures in a 1000-ml. stainless steel autoclave. Usual precautions were observed to ensure exclusion of air from the reaction mixture, by initial flushings with dry nitrogen.

ψ'-Heptyl Hydride. Method A.[16,17]—The following charge reacted for 24 hours at 180–190°: 100 g. (0.23 mole) of ψ'-heptyl iodide, 180 g. (1.43 moles) of sodium sulfite, 180 g. of water, 0.68 g. of aniline and 1.44 g. of trisodium phosphate decahydrate. The cooled reaction mixture, black with sulfur and metallic sulfides, was steam distilled to give 34 g. of dense oil, which after percolation through Florisil and distillation gave 21 g. (33%) of ψ'-heptyl hydride, b.p. 108–110°, n^{20}_{D} 1.298, d^{20}_{4} 1.609 and 7 g. (5%) of crude ψ'-heptyl mercaptan, b.p. 64–65° (20 mm.), n^{20}_{D} 1.3390, d^{20}_{4} 1.673. Further purification gave products with properties shown in Table I.

ψ'-Heptyl Hydride. Method B.[18]—A charge of 176.8 g. (0.4 mole) of ψ'-heptyl iodide, 33.6 g. (0.2 mole) of sodium sulfide pentahydrate and 150 g. of water reacted for 24 hours at 250°. The cooled reaction mixture was extracted with 1 lb. of ether. Following successive washes with water, 2% bicarbonate solution and water, the ether extract was dried and distilled to give 23.7 g. (18.7%) of ψ'-heptyl hydride.

ψ'-Heptyl Hydride. Method C.—Conventional procedures were used for the reduction of 106.1 g. (0.24 mole) of ψ'-heptyl iodide with 6 g. (0.16 mole) of lithium aluminum hydride[29,30] in ether. The iodide was added over a 2-hour period, and the reaction mixture was stirred an additional 30 minutes. Following the usual work-up, distillation of the neutral, dry ether extract gave 34 g. (45%) of ψ'-heptyl hydride, together with 39 g. (37%) of ψ'-heptyl iodide.

Thermal Reaction of ψ'-Heptyl Iodide with Sulfur.—A mixture of 177.0 g. (0.4 mole) of ψ'-heptyl iodide and 12.0 g. (0.37 mole) of sulfur reacted for 24 hours at 250–270°. Cooled contents of the autoclave were extracted with 1 lb. of ether. Following washes with 1 *N* aqueous sodium thiosulfate to remove iodine, the ether extract was water washed, dried and distilled to give 6 g. (3%) of ψ'-heptyl iodide, 25 g. (20%) of crude bis-(ψ'-heptyl), b.p. 134–138° (20 mm.), 59 g. (44%) of crude bis-(ψ'-heptyl) sulfide, b.p. 155–165° (20 mm.), and 10 g. (10%) of crude bis-(ψ'-heptyl) disulfide, b.p. 165–175° (20 mm.). Careful fractionation of the crude bis-(ψ'-heptyl) gave the pure product reported in Table I. Reduction by published procedures[31] of 46.4 g. of the crude bis-(ψ'-heptyl) sulfide fraction and 10 g. of the crude bis-(ψ'-heptyl) disulfide fraction with 5.7 g. (0.15 mole) of lithium aluminum hydride, followed by distillation, gave 29 g. of bis-(ψ'-heptyl) sulfide and 10 g. of ψ'-heptyl mercaptan, having properties and analyses shown in Table I.

Thermal Reaction of ψ'-Heptyl Iodide with Selenium.—A charge of 442.0 g. (1.0 mole) of ψ'-heptyl iodide and 73.0 g. (0.93 mole) of selenium reacted for 24 hours at 260°. Extraction of the cooled reaction products with 2 lb. of ether and subsequent titration with 1 *N* aqueous sodium thiosulfate indicated a 60% reaction of the ψ'-heptyl iodide. Distillation of the dried ether extract furnished 155 g. (35%) of ψ'-heptyl iodide, 159 g. (45% or 69% conversion based on reacted ψ'-heptyl iodide) of crude bis-(ψ'-heptyl) selenide, b.p. 140–160° (10 mm.), and 23 g. (6%) of crude bis-(ψ'-heptyl) diselenide, b.p. 160–180° (10 mm.). The crude selenide and diselenide fractions were reduced with 11.4 g. (0.3 mole) of lithium aluminum hydride by conventional procedures.[31] Selenomercaptides were removed from the resulting ether extract by repeated washings with 0.5 *N* potassium hydroxide. Acidification of the caustic washings gave a heavy oil which distilled at 170–175° (10 mm.), and which, after percolation through Florisil, had the properties of bis-(ψ'-heptyl) diselenide reported in Table I. Distillation of the dried ether extract gave 120 g. of fairly pure bis-(ψ'-heptyl) selenide, b.p. 145–153° (10 mm.), n^{20}_{D} 1.346–1.348. This crude product was reduced by stirring 3 hours at 80–95° in a mixture of 7 g. of zinc and 25 ml. of 40% sodium hydroxide. This procedure removed the contaminating diselenide as $H(CF_2)_6CH_2SeNa$ (sodium 1H,1H,7H-dodecafluoroheptyl selenomercaptide). Extraction with ether and subsequent distillation gave 92 g. of the analytically pure sample reported in Table I.

Thermal Reaction of ψ'-Undecyl Iodide with Selenium.—A charge of 225 g. (0.35 mole) of ψ'-undecyl iodide and 23.0 g. (0.3 mole) of selenium was heated for 24 hours at 260°. Following extraction with ether, titration with standard thiosulfate indicated a 50% reaction of the iodide. Distillation of the ether extract yielded 100 g. (44%) of the initial ψ'-undecyl iodide and 73 g. (38% yield or 68% conversion based on the reacted ψ'-undecyl iodide) of bis-(ψ'-undecyl) selenide, b.p. 165–175° (0.6 mm.), m.p. 91–93°. Processing this latter fraction by the zinc–caustic treatment of the preceding example and subsequent redistillation gave the pure bis-(ψ'-undecyl) selenide reported in Table I.

Coupling Reaction of ψ'-Heptyl Iodide with Zinc and Acetic Anhydride.—A mixture of 88.4 g. (0.20 mole) of ψ'-heptyl iodide, 13.7 g. (0.21 mole) of granular zinc, 45.9 g. (0.45 mole) of acetic anhydride and 100 ml. of methylene chloride was refluxed for 25 hours, according to Henne's procedure for coupling perfluoroalkyl iodides.[27] Work-up and drying gave a single organic phase which distilled to give 35 g. (56%) of bis-(ψ'-heptyl), b.p. 134–136° (20 mm.). Redistillation furnished 23 g. of product with properties identical with those of the bis-(ψ'-heptyl) obtained by the thermal reaction of ψ'-heptyl iodide with sulfur.

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