1-Hydroxyfluorene-1-C^{14}.—1,2,3,4-Tetrahydrofluoren-1-one-1-C^{14} (0.560 g., 3.04 mmoles) was dehydrogenated according to the method described by Morgan and Gutmann,[5] except dichloromethane instead of ether was used in the extraction of the crude reaction mixture. There was obtained 0.414 g. (2.27 mmoles, 75% yield) of 1-hydroxyfluorene-1-C^{14}.

1-Hydroxy-2-nitrofluorene-1-C^{14}.—1-Hydroxyfluorene-1-C^{14} (0.414 g., 2.27 mmoles) was nitrated by the procedure reported by Weisburger and Weisburger.[8] Chromatography of the crude nitration product on alumina (Merck, acid-washed) gave 0.211 g. (0.93 mmole, 41% yield) of 1-hydroxy-2-nitrofluorene-1-C^{14}.

1-Hydroxy-2-aminofluorene-1-C^{14} Hydrochloride.—1-Hydroxy-2-nitrofluorene-1-C^{14} (0.211 g., 0.93 mmole) was reduced[8] with zinc dust. The hot reaction mixture was filtered through Celite into 1.9 ml. of concd. hydrochloric acid, and the zinc was washed with ethanol. The filtrate and washings were combined and the ethanol was removed under reduced pressure at 40°. The mixture was then cooled in an ice bath, and the product was transferred to a sintered glass funnel with the aid of a small volume of ice-cold concd. hydrochloric acid. After drying *in vacuo* over potassium hydroxide, there was obtained 0.159 g. (0.68 mmole, 73%) of 1-hydroxy-2-aminofluorene-1-C^{14} hydrochloride.

***N*-(1-Hydroxy-2-fluorenyl-1-C^{14})acetamide.**—The hydrochloride of 1-hydroxy-2-aminofluorene-1-C^{14} (0.159 g., 0.68 mmole) was acetylated by the method of Weisburger and Weisburger,[8] yielding 0.160 g. (0.67 mmole, 99%) of crude *N*-(1-hydroxy-2-fluorenyl-1-C^{14})acetamide. Chromatography of the crude product on alumina (Merck, acid-washed) with ethyl acetate as eluent, followed by recrystallization from dilute ethanol, gave 0.126 g. (0.529 mmole, 78% yield) of *N*-(1-hydroxy-2-fluorenyl-1-C^{14})acetamide as white needles, m.p. 211–212° (reported[8] m.p. 208°), after drying *in vacuo* at 78° over phosphoric anhydride. The specific radioactivity of the *N*-(1-hydroxy-2-fluorenyl-1-C^{14})acetamide was 4.99 mc. per mmole.

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Asymmetric Synthesis of (+)-Bicyclo[2.2.2]octanol-2[1]

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Brown and Zweifel[2] have recently reported that they obtained nearly complete asymmetric stereoselectivity[3] by the addition of diisopinocampheylborane to various olefines. This remarkable achievement prompted us to apply this method to the synthesis of optically active bicyclo[2.2.2]octanol-2.

We wish to report that the addition of diisopinocampheylborane (from (−)-α-pinene) to bicyclo[2.2.2]octene-2 produced *S*-(+)-bicyclo [2.2.2]octanol,[4] m.p. 214–217°, $[\alpha]^{25}\text{D}$ +6.9° (*c* 2.37, chloroform).

Based on the known absolute configuration[5] of (−)-α-pinene and by the application of the Prelog-Cram rule[6] one would predict the *R* configuration for the resulting alcohol. This was not found to be the case and is therefore inconsistent with the absolute configurational assignment of *S*-(+)-bicyclo[2.2.2]octanol-2 which has been determined by a different method.[4]

Experimental[7]

***S*-(+)-Bicyclo[2.2.2]octanol-2.**—To a solution of 3.12 g. (0.083 mole) of sodium borohydride in 75 cc. of anhydrous diglyme was added 27.2 g. of α-pinene,[8] $[\alpha]^{25}\text{D}$ −47.88. The solution was cooled to 0° and while under an atmosphere of argon 14.2 g. of freshly distilled boron trifluoride-etherate was added at a rate which maintained the temperature between 0–5°. The mixture was stirred for an additional hour at 0–2° and then 10.4 g. (0.1 mole) of bicyclo[2.2.2]-octane-2[9] was added. Stirring was continued for 4 hr. at 0–2° and finally at room temperature for 12 hr.

The reaction mixture was hydrolyzed by the addition of water, 31 cc. of 3 *N* sodium hydroxide and finally, 31 cc. of 30% hydrogen peroxide at a sufficient rate so that the temperature of the solution was kept between 30–35°. The reaction mixture was extracted with pentane, and the extract was washed with water and dried over anhydrous magnesium sulfate. The solvent was removed and the residue distilled at 85 mm. to yield 3.55 g. of material, b.p. 60–75°. Fractional sublimation of the waxy product gave fractions, the specific rotations of which varied from +6 to +7°. Recrystallization of the sublimed material from pentane yielded 2.61 g. of bicyclo[2.2.2]octanol-2, m.p. 214–217° (s.t.), $[\alpha]^{28}\text{D}$ +6.9° (*c* 2.32, chloroform), the infrared spectrum of which was identical with that of an authentic sample. Vapor phase chromatography showed that the sample was not contaminated with isopinocampheol. Recrystallization of the residue from the above distillation yielded an additional 1.04 g. of alcohol, $[\alpha]^{28}\text{D}$ +6.3° (*c* 2.15, chloroform) making the total yield of alcohol 30%.

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(1) This work was supported by a Research Grant CY-4065, National Institute of Health, Public Health Service.

(2) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 486 (1961).

(3) A comparable degree of stereoselectivity has been previously reported [J. A. Berson and M. A. Greenbaum, *ibid.*, **80**, 445 (1958)] in an atrolactic acid synthesis.

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(7) Melting points and boiling points are uncorrected.

(8) We wish to thank Prof. H. C. Brown, Purdue University and the Glidden Co., Jacksonville, Fla., for supplying us with generous samples of α-pinene.

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Some Free Radical-Catalyzed Additions of Perfluoroalkyl Iodides to Olefins

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The free radical-catalyzed addition of one- and two-carbon perhaloalkyl iodides to simple olefins has been investigated extensively, principally by Haszeldine.[1] The work presently reported demonstrates that this synthetic method can be extended successfully by use of longer-chain perfluoroalkyl iodides and by functional substitution in the olefin.

Organic peroxides and azobisnitriles are known as highly effective initiators for free radical additions. However, for this investigation ultraviolet irradiation was employed, in order not to introduce minor amounts of side products derived from the initiator; it could be anticipated that the high-boiling desired products might thus be more readily purified. The penalty one pays for this choice is that there is a progressive loss of effective radiation, resulting in incomplete reaction. Reasons for this are that the reaction mixtures tend to darken during the run, and also that the ultraviolet absorption maxima of the products lie only *ca.* 50 Å to shorter wavelengths than that of the starting compound, *n*-perfluoroheptyl iodide. Inasmuch as the relatively low-boiling starting materials were, as expected, readily separable from the desired products, such behavior was here of little concern. For the preparation of the easily distillable adduct of n-C_3F_7I to isobutene, benzoyl peroxide was employed and the reaction proceeded to completion. In a similar addition of dibromodifluoromethane to isobutene an error in the literature was uncovered.

The adducts of perfluoroalkyl iodides to olefins are known to be readily dehydrohalogenated by bases.[2] Some semiquantitative information is given to illustrate the reactivity of the higher molecular weight adducts prepared in this investigation.

Experimental

Materials.—The perfluoro-*n*-heptyl iodide was prepared as has been described.[3] It had n^{25}D 1.3339, not 1.3274 as erroneously given;[3] its ultraviolet absorption spectrum (4.0 mg./ml. isooctane) had λ_{max} 2720 Å, ϵ_{max} 282, and band width at half-height, $W_{1/2}$ 6300 cm.$^{-1}$. Preparation and properties of perfluoro-*n*-propyl iodide have been presented.[4] Octene-1 and octadecene-1 were obtained from the Connecticut Hard Rubber Co., undecylenic acid from the Baker Castor Oil Co., and vinylmethyldiethoxysilane from the Linde Air Products Co. All were vacuum distilled before use, and had n^{25}D 1.4060, 1.4425, 1.4475, and 1.3973, respectively.

1-Perfluoroheptyl-2-iodooctane.—In a stoppered 50-ml. Pyrex test tube equipped with 6-mm. i.d. air condenser was placed n-$C_7F_{15}I$, 20.0 g. (0.04 mole) and octene-1, 4.50 g. (0.04 mole). The reaction mixture was externally irradiated for 15 hr. by an unfiltered "Hanovia" quartz-mercury arc lamp placed at a distance of 6 in. from the test tube. Upon fractional distillation of the mixture the desired adduct, n-$C_7F_{15}CH_2CHIC_6H_{13}$, b.p. 156°/20 mm. n^{25}D 1.3846, was obtained in 87% yield, as calculated on the basis of "conversion," 60% (*i.e.*, $C_7F_{15}I$ not recovered).

Anal. Calcd. for $C_{15}H_{16}F_{15}I$: C, 29.62, F, 46.86; I, 20.87. Found: C, 29.8; F, 46.8; I, 20.8.

Its ultraviolet spectrum in isooctane had λ_{max} 2663 Å, ϵ_{max} 483 and $W_{1/2}$ 5050 cm.$^{-1}$.

1-Perfluoroheptyl-2-iodooctadecane.—Octadecene-1, 0.03 mole, and n-$C_7F_{15}I$, 0.03 mole, were treated as above. The adduct, n-$C_7F_{15}CH_2CHIC_{16}H_{33}$, isolated by vacuum distillation, had b.p. 170–200°/0.01 mm. and n^{25}D 1.4107. The yield was 93%, based on 71% conversion of n-$C_7F_{15}I$.

Anal. Calcd. for $C_{25}H_{36}F_{15}I$: I, 16.96. Found: I, 16.7.

10-Iodo-11-perfluoroheptylhendecanoic Acid.—From undecylenic acid, 0.03 mole, and n-$C_7F_{15}I$, 0.03 mole, the above-described procedure gave n-$C_7F_{15}CH_2CHI(CH_2)_8$-CO_2H, b.p. 190–240°/0.01 mm. m.p. 50–51°, (recryst. from cyclo-$C_8F_{16}O$) in a yield of 73% based upon 44% conversion of n-$C_7F_{15}I$.

Anal. Calcd. for $C_{18}H_{20}F_{15}IO_2$: C, 31.78; F, 41.90; I, 18.66. Found: C, 31.8; F, 42.1; I, 18.2.

2,2-Diethoxy-3-iodo-4-perfluoroheptyl-2-silabutane.—Vinylmethyldiethoxysilane, 0.04 mole, and n-$C_7F_{15}I$, 0.04 mole, treated in the above fashion, produced $C_7F_{15}CH_2$-$CHISi(CH_3)(OC_2H_5)_2$, b.p. 150°/20 mm., n^{25}D 1.3795, the yield being 62% based on 37% conversion of n-$C_7F_{15}I$.

Anal. Calcd. for $C_{14}H_{16}F_{15}IO_2Si$: C, 25.66; F, 43.49; I, 19.37. Found: C, 25.5; F, 43.2; I, 19.15.

The ultraviolet spectrum in isooctane had λ_{max} 2685 Å, ϵ_{max} 484, $W_{1/2}$ 5500 cm.$^{-1}$.

1-Perfluoropropyl-2-iodo-2-methylpropane.—Isobutene, 5.7 g. (0.10 mole), n-C_3F_7I, 30.0 g. (0.10 mole), and benzoyl peroxide, 1.0 g., were treated for 6 hr. at 90° in a 43-ml. rocking autoclave. Upon fractional distillation of the product there was obtained n-$C_3F_7CH_2CI(CH_3)_2$, b.p. 63°/40 mm., n^{25}D 1.3963, the yield being 91%, based upon 100% conversion of the perfluoropropyl iodide.

Anal. Calcd. for $C_7H_8F_7I$: C, 23.95; F, 37.60; I, 36.15. Found: C, 24.2; F, 37.9; I, 35.9.

Adduct of CF_2Br_2 to Isobutene.—This compound, $C_5H_8Br_2$-F_2, was reported[5] to have n^{25}D 1.4632. When prepared as above, except that ditertiary butyl peroxide was used and the reaction temperature was 140°, the adduct had b.p. 69°/40 mm., in excellent agreement with the literature value,[5] but had n^{25}D 1.4527. Presumably a typographical error was responsible for the discrepancy. Although the cited reference[5] did not mention the formation of telomeric materials, it appears that appreciable 1:2 adduct was formed (about one-fifth as much as the simple adduct); it was not stable under the conditions of handling and eliminated hydrogen bromide. The resulting olefin was principally $BrCF_2CH_2C(CH_3)_2CH{=}C(CH_3)_2$, as indicated by the infrared spectrum. It had b.p. 93°/40 mm. and n^{25}D 1.4414.

Anal. Calcd. for $C_9H_{15}BrF_2$: Br, 33.2. Found: Br, 32.4.

Dehydrohalogenation Studies.—Percentage dehydroiodination of the octene, octadecene, and vinylsilane adducts, measured *via* iodide ion liberated upon 1-hr. reflux in 90% ethanolic potassium bicarbonate (0.01 *M*) were, respectively, 61%, 39%, and 96%. When potassium carbonate was used, values for the latter two adducts were 68% and 99%. Upon treatment for 16 hr. at 25°, the vinylsilane adduct reacted to the extent of 92% with potassium carbonate, but less than 7% with potassium bicarbonate.

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