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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[8] E. K. Weisburger and J. H. Weisburger, *J. Org. Chem.*, **19**, 964 (1954).

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

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Received December 20, 1961

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°, $[\alpha]^{25}$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] $[\alpha]^{25}$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.), $[\alpha]^{28}$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, $[\alpha]^{28}$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.

[4] H. M. Walborsky, M. E. Baum, and A. A. Youssef, *J. Am. Chem. Soc.*, **83**, 988 (1961).

[5] A. J. Birch, *Annual Rep. Prog. Chem.*, **47**, 191 (1950).

[6] D. J. Cram and F. A. Abd Elhafez, *J. Am. Chem. Soc.*, **74**, 5828 (1952); V. Prelog, *Helv. Chim. Acta*, **36**, 308 (1953).

[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.

[9] H. M. Walborsky and D. F. Loncrini, *J. Am. Chem. Soc.*, **76**, 5396 (1954).

Some Free Radical-Catalyzed Additions of Perfluoroalkyl Iodides to Olefins

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Contribution No. 227 from the Central Research Department of the Minnesota Mining and Manufacturing Co., St. Paul 19, Minn.

Received December 20, 1961

The free radical-catalyzed addition of one- and two-carbon perhaloalkyl iodides to simple olefins has been investigated extensively, principally