# Fluorination of Norbornadiene and 1,4-Dihydro-1,4-methanonaphthalene with Substituted (Difluoroiodo)benzenes

By **Ana Gregorčič** and **Marko Zupan,**\* Department of Chemistry and J. Stefan Institute, University of Ljubljana, Yugoslavia

The reaction of substituted (difluoroiodo)benzenes with norbornadiene results in four products: 3-*exo*,5-*endo*- (2) (49—55%), 3-*exo*,5-*exo*- (3) (15—20%), and 3-*endo*,5-*endo*-difluorotricyclo[2.2.1.0²,⁶]heptane (4) (6—8%), and 5-*exo*,7-*syn*-difluoronorborn-2-ene (5) (18—32%), depending upon the substituent in the benzene ring. The reaction with 1,4-dihydro-1,4-methanonaphthalene results in 2-*exo*,9-*syn*-difluoro-1,4-dihydro-1,4-methanonaphthalene.

ADDITION of chlorine to olefinic double bonds with (dichloroiodo)benzene has received attention from several workers.[1-4] The corresponding (difluoroiodo)benzenes have received more limited attention as fluorinating agents, possibly because of the difficulties involved in their preparation and storage. Three reported

that hydrogen fluoride or another strong acid such as trifluoroacetic acid, is necessary as a catalyst in the fluorination reaction and proposed an ionic mechanism. On the other hand, we have recently found [13-15] that difluoroiodomethane reacts with phenylalkenes in the presence of hydrogen fluoride as catalyst to form the



$$X = H, p-OMe, m-Cl, or\ m-NO_2$$
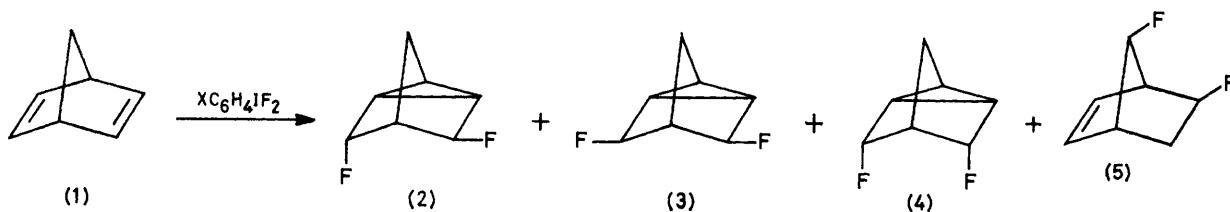
SCHEME 1

methods [5-8] are of particular interest for the preparation of (difluoroiodo)arenes. We have developed a further method using xenon difluoride as fluorinating agent in dichloromethane solution and in the presence of a catalytic amount of hydrogen fluoride at room temperature.[9]

The reactions of norbornene have been utilized for elucidating the mechanism and the stereochemistry of various reactions.[10] However, halogenations of norbornadiene have been studied much less intensively. Winstein [11] has studied the bromination of this system and has pointed out that the products may have dangerous properties. We now report a study of the fluorination of norbornadiene and its benzo-analogue 1,4-dihydro-1,4-methanonaphthalene with substituted (difluoroiodo)benzenes.

RESULTS AND DISCUSSION

(Difluoroiodo)arenes have already been used for fluorination of 1,1-diphenylethylene [12] and styrene,[8] giving gem-difluoro-compounds. Carpenter [8] showed

corresponding 1-fluoro-2-iodo-1-phenylalkanes and not the rearranged gem-difluoro-compounds.

The reaction of (difluoroiodo)benzene (X = H) with norbornadiene (1) results in four major and two minor (unidentified) products (Scheme 1), which could be separated by preparative g.l.c. and which were identified on the basis of their mass and ^{19}F and [1]H n.m.r. spectra and chemical transformations. The products (2)—(4) have similar mass spectra with little differences in peak intensities of the fragments $m/e$ 130 ($M^+$), 105, 109, 97, 84, and 79; the product (5) has the same molecular ion peak, $m/e$ 130, but different fragments. The similarity in mass spectra indicates that the products (2)—(4) are isomers. The product (2) shows in its [19]F n.m.r. spectrum two doublets at −201.8 and −213 p.p.m., corresponding to the exo- and endo-fluorine atoms, and in its [1]H n.m.r. spectrum two doublets at lower field (δ 5.2 and 4.74, corresponding to exo- and endo-protons). The product (3) shows in its [19]F n.m.r. spectrum one doublet at −201.4 p.p.m., corresponding to the exo-fluorine atom

[1] D. F. Banks, *Chem. Rev.*, 1966, **66**, 243.

[2] D. H. R. Barton and E. Miller, *J. Amer. Chem. Soc.*, 1950, **72**, 370.

[3] S. J. Cristol, F. R. Stermitz, and P. S. Ramey, *J. Amer. Chem. Soc.*, 1956, **78**, 4939.

[4] D. D. Tanner and G. C. Gidley, *J. Org. Chem.*, 1968, **33**, 38.

[5] O. Dimroth and W. Bockemüller, *Ber.*, 1931, **64**, 516, 522.

[6] B. S. Garvey, jun., L. F. Halley, and C. F. Allen, *J. Amer. Chem. Soc.*, 1937, **59**, 1827.

[7] H. Schmidt and H. Meinert, *Angew. Chem.*, 1960, **72**, 109.

[8] W. Carpenter, *J. Org. Chem.*, 1966, **31**, 2688.

[9] M. Zupan and A. Pollak, *J. Fluorine Chem.*, 1976, **7**, 445.

[10] R. C. Fahey, *Topics Stereochem.*, 1968, **3**, 237; J. A. Borson, in 'Molecular Rearrangements,' vol. 1, Part 2, ed. P. de Mayo, Interscience, New York, 1963, p. 111; T. G. Traylor, *Accounts Chem. Res.*, 1969, **2**, 152.

[11] S. Winstein, *J. Amer. Chem. Soc.*, 1961, **83**, 1516.

[12] J. Bornstein, M. R. Borden, F. Nunes, and H. I. Tarlin, *J. Amer. Chem. Soc.*, 1963, **85**, 1609.

[13] M. Zupan and A. Pollak, *Tetrahedron Letters*, 1975, 3576.

[14] M. Zupan and A. Pollak, *J. Org. Chem.*, 1976, **41**, 2179.

[15] M. Zupan and A. Pollak, *J.C.S. Perkin I*, 1976, 1745.

and in its $^1$H n.m.r. spectrum a doublet at lower field ($\delta$ 4.53, corresponding to the two *endo*-protons). The product (4) shows in its $^{19}$F n.m.r. spectrum one doublet of multiplets at $-201.8$ p.p.m., corresponding to *endo*-fluorine and in its $^1$H n.m.r. spectrum a doublet of multiplets at lower field ($\delta$ 4.92), corresponding to the two *exo*-protons. On the basis of the above data, we have identified the products as the tricyclic difluoroderivatives (2)—(4). The product (5) shows in its $^{19}$F n.m.r. spectrum one doublet of doublets at $-180$ p.p.m. and one multiplet at $-187.5$ p.p.m. and in its $^1$H n.m.r. spectrum three signals at lower field: a multiplet at $\delta$ 6 (two vinyl protons), a doublet of triplets at $\delta$ 4.74 ($J$ 57 and 3 Hz), and a doublet at $\delta$ 4.6 ($J$ 60 Hz), in agreement with the 5-*exo*,7-difluoronorborn-2-ene structure (5). However, from the data just described we were unable to make a decision about the stereochemistry at C-7. In order to establish this, we converted the product into the previously synthesized 2-*exo*,7-*syn*-difluoronorbornane [16] by catalytic hydrogenation.

The reaction of 1-chloro-4-(difluoroiodo)benzene with the methanonaphthalene (6) results in one product (Scheme 2). The structure (7) was assigned on the basis of its mass and $^1$H and $^{19}$F n.m.r. spectra. The product shows in its $^{19}$F n.m.r. spectrum two signals: a multiplet at $-182.25$ p.p.m. and a doublet of doublets at $-183$ p.p.m., and in its $^1$H n.m.r. spectrum two proton signals at lower field: a doublet of multiplets at $\delta$ 4.75 and a doublet at $\delta$ 4.7. The mass spectrum shows fragmentations, similar to those of 5-*exo*,7-*syn*-difluoronorborn-2-ene (5) and also to 2-*exo*,7-*syn*-, and 2-*exo*,7-*anti*-difluoronorbornane prepared earlier.[16] The major peaks are at $m/e$ 147 ($M^+ - CH_2F$), 134 ($M^+$



(6)                              (7)
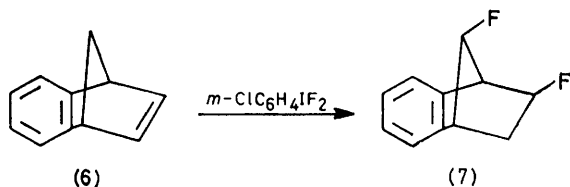
SCHEME 2

$- C_2H_3F$), 133 ($M^+ - C_2H_4F$), and 129 ($M^+ - CHF_2$). The $^{19}$F n.m.r. signal corresponding to the C-7 fluorine atom ($-183$ p.p.m.) occurs *ca.* 50 p.p.m. to lower field than those of 2-*exo*,7-*syn*- and 2-*exo*,7-*anti*-difluoronorbornane. However, when we compare the n.m.r. data with those of the product (5), whose structure was already confirmed by hydrogenation, we observe very similar chemical shifts for fluorine atoms, and signals for hydrogen atoms at lower field. On the basis of $^1$H and $^{19}$F n.m.r. spectra the structure (7) was established.

We studied the effect of groups bonded to the benzene ring on the distribution of products of reactions of norbornadiene with substituted (difluoroiodo)benzenes. The product ratios were estimated by g.l.c. Each reaction was repeated several times, and the average results

[16] D. D. Tanner and P. Van Bostelen, *J. Amer. Chem. Soc.*, 1972, **94**, 3187.

are presented in the Table. We observed no isomerization of the products under the reaction and isolation conditions. The results show that differences in electronegativity of the group bonded to the benzene ring can alter the proportions of the products (2) and (3) by *ca.*

Variations in composition of products from addition of (difluoroiodo)arenes to norbornadiene at 25 °C

| X | Products (%) | | | |
| | (2) | (3) | (4) | (5) |
|---|---|---|---|---|
| *p*-OMe | 55 | 20 | 7 | 18 |
| H | 51 | 17 | 6 | 32 |
| *m*-Cl | 48 | 17 | 8 | 27 |
| *m*-NO$_2$ | 49 | 15 | 7 | 29 |

5—6%, of the product (4) by only 2%, and of the product (5) by *ca.* 14%.

The formation of a single product from the benzo-analogue (6) could be explained in terms of reaction with a polarized complex of (difluoroiodo) with hydrogen fluoride, thus forming the ion (A) (Scheme 3), which undergoes Wagner–Meerwein rearrangement forming in turn the intermediate (B). Dissociation of the carbon-iodine bond results in the ion (C) ($S_N1$), which could, after nucleophilic attack, yield the products (7) and (7a). The formation of (7a) could also be interpreted in terms of $S_N2$ nucleophilic substitution of the aryliodine function. However, we have not observed such a product, and for this reason we suggest an intramolecular substitution pathway, involving the intermediate (D), formed by hydrogen-fluoride-induced polarization of the F–I bond in the intermediate (B), resulting in only one product (7).

The formation of four products from norbornadiene is shown diagrammatically in Scheme 4. The (difluoroiodo)-arene molecules, polarized by hydrogen fluoride, could yield ions (E) or (F) by *exo*- or *endo*-attack on the double bond, resulting in the product (5) after Wagner–Meerwein rearrangement. As we cannot say whether an *exo*- or an *endo*-cation will undergo Wagner–Meerwein rearrangement, the formation of (5) is preferably explained by $S_N2$ substitution of the aryliodine function or by above-mentioned intramolecular substitution. The first-formed ions (E) and (F) could give the products (2)—(4) *via* the intermediate species (G)—(J), after $S_N1$ or $S_N2$ substitution of the aryliodine function by a fluoride ion or by the above-mentioned intramolecular substitution. Evidence for phenyliodonium salts such as (B) (G), (H), and (I) has been reported.[17] An attempt to isolate phenyliodonium salts, which could provide stronger evidence for the suggested intramolecular substitution, is in progress.

## EXPERIMENTAL

I.r. spectra were recorded with a Perkin-Elmer 257 spectrometer, and $^1$H and $^{19}$F n.m.r. spectra with a JEOL JNM-P2-100 instrument for solutions in $CCl_4$ with Me$_4$Si or $CCl_3F$ as internal reference. Mass spectra (including high resolution) were taken with a CEC-21-110 spectro-

[17] P. G. Holton, A. D. Cross, and A. Bowers, *Steroids*, 1963, **2**, 71.

meter. G.l.c. was carried out on a Varian Aerograph 1800 instrument.

*Materials.*—Commercially available norbornadiene was purified by g.l.c. before use, and benzonorbornene was prepared as described in ref. 18. Substituted iodobenzenes were prepared by known methods from corresponding amino-derivatives and distilled before use. Dichloro-

was analysed by g.l.c. (Carbowax 20M–25% Varaport 70—80; 160 °C). The products were separated by preparative g.l.c.

*Norbornadiene.* Preparative g.l.c. (Carbowax 20M–25% Varaport 30 70—80; 160 °C) gave 3-endo,5-exo-*difluoro-tricyclo*[2.2.1.0$^{2,6}$]*heptane* (2) (38%), waxy solid, m.p. (sealed capillary) 75—76 °C, $\delta_F$ (CCl$_4$) —201.8 (d, $J_{FH}$ 60
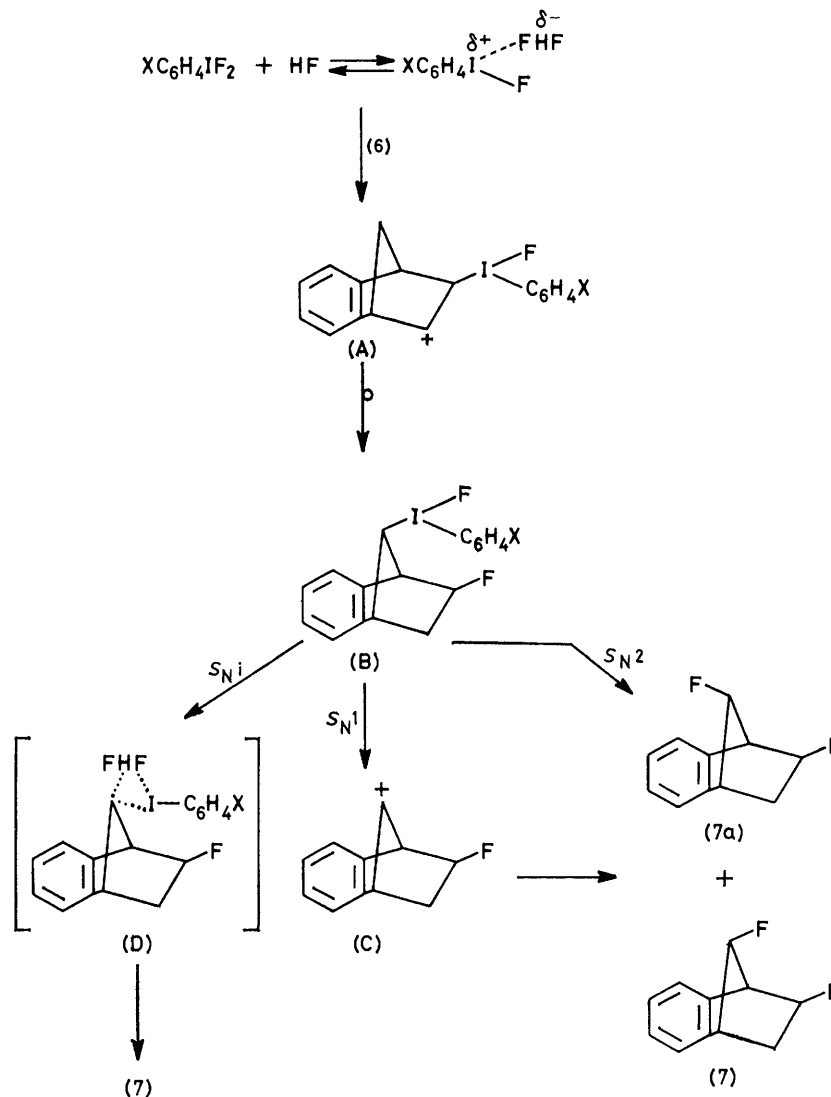


SCHEME 3

methane was purified [19] and stored over molecular sieves. Hydrogen fluoride (Fluka purum) was used and xenon difluoride was prepared by the photosynthetic method [20] with a purity of >99.5%. Substituted (difluoroiodo)benzenes were prepared as described in ref. 9.

*General Procedure for Fluorination with Substituted (Difluoroiodo)benzenes.*—To a stirred solution of the (difluoroiodo)arene (1.1 mmol) in dichloromethane (5 ml), the olefin (1 mmol) was added at room temperature. After 2 h, the mixture was diluted with dichloromethane (15 ml), washed (10 ml of 5% NaHCO$_3$; 10 ml of H$_2$O), dried (Na$_2$SO$_4$), filtered, and evaporated *in vacuo*, and the residue

Hz *exo*-F) and —213 p.p.m. (d, $J_{FH}$ 60 Hz, *endo*-F), $\delta_H$ 5.22 (d, *exo*-H), and 4.74 (d, *endo*-H), *m/e* 130 ($M^+$, 58%), 115 (53), 109 (30), 97 (100), 84 (35), and 79 (65) (Found: C, 64.65; H, 6.1%; $M^+$, 130.059 7. C$_7$H$_8$F$_2$ requires C, 64.6; H, 6.2%; $M$, 130.059 4); 3-exo,5-exo-*difluoro-tricyclo*[2.2.1.0$^{2,6}$]*heptane* (3) (10%), waxy solid, m.p. (sealed capillary) 76—77 °C; $\delta_F$ (CCl$_4$) —201.4 p.p.m. (d), δ 4.53 (d) ($J_{FH}$ 60 Hz); *m/e* 130 ($M^+$, 35%), 115 (45), 109 (25), 97 (100), 84 (38), and 79 (57) (Found: C, 64.35; H, 5.95%; $M^+$, 130.059 7); 3-endo,5-endo-*difluorotricyclo*-[2.2.1.0$^{2,6}$]*heptane* (4%), solid, m.p. (sealed capillary) 86—

[18] L. Friedman and F. M. Logullo, *J. Amer. Chem. Soc.*, 1963, **85**, 1549.

[19] 'Techniques of Organic Chemistry,' vol. VII, ed. A. Weissberger, Interscience, New York, 1955.
[20] S. M. Williamson, *Inorg. Synth.*, 1968, **11**, 147.

88 °C, $\delta_F$ (CCl$_4$) −201.8 p.p.m. (dm), $\delta_H$ 4.92 (dm) ($J_{FH}$ 60 Hz); $m/e$ 130 ($M^+$, 36%), 115 (38), 109 (39), 97 (76), 84 (25), and 79 (100) (Found: C, 64.9; H, 6.45%; $M^+$, 130.058 9); and 5-exo,7-syn-*difluoronorborn-2-ene* (5) (20%), waxy solid, m.p. (sealed capillary) 82—83 °C, $\delta_F$ (CCl$_4$)

tributions are in the Table. To test the stability of the difluorides under the reaction conditions, a sample (0.1 g) containing products (2)—(5) was added to dichloromethane; traces of hydrogen fluoride and (difluoroiodo)benzene (0.2 mmol) were then added, and the mixture was stirred at 20 °C
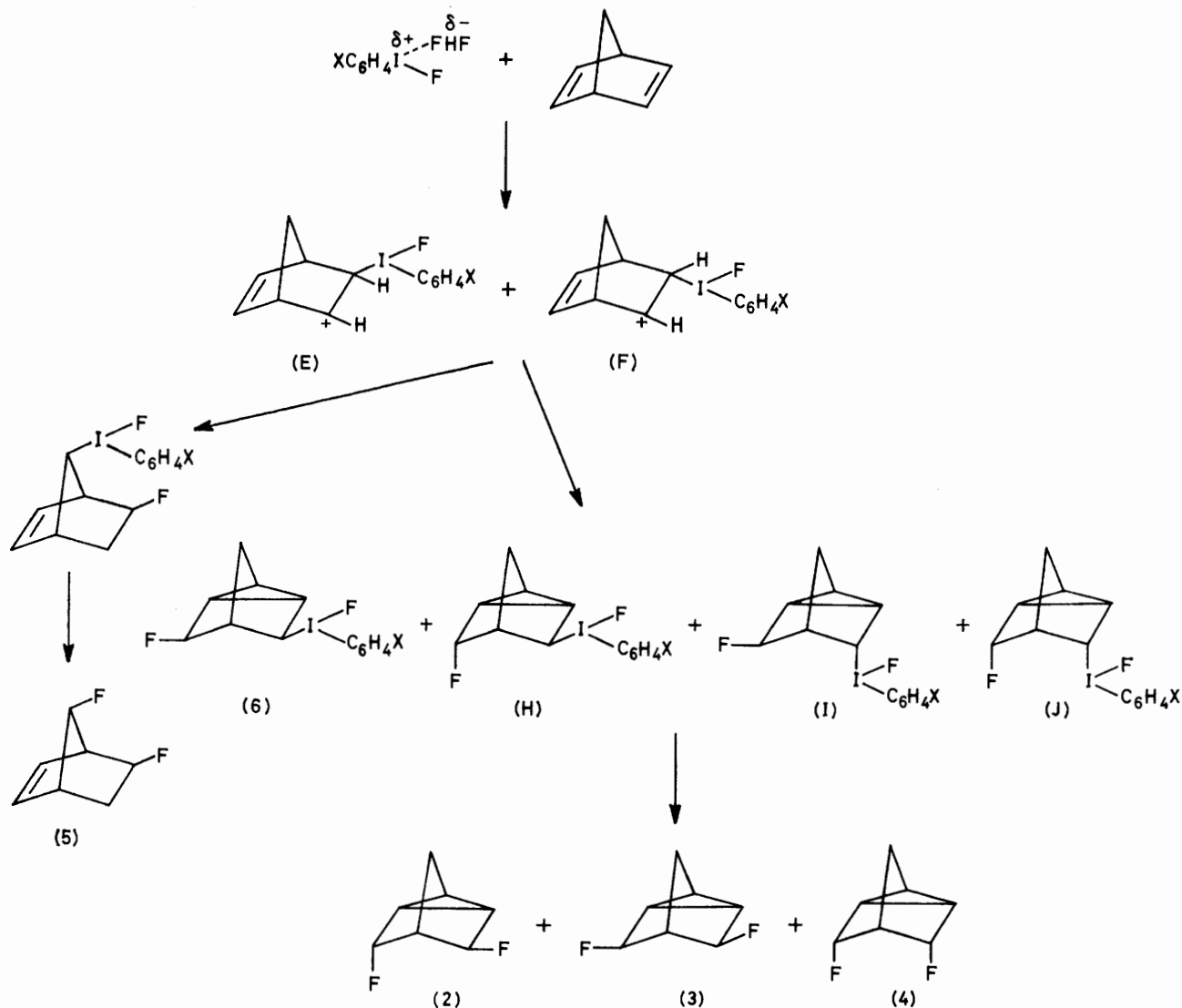


Scheme 4

−187.5 (m, F-5) and −180 p.p.m. (dd, F-7), $\delta_H$ 4.74 (dt, H-5), 4.6 (d, H-7), and 6.0 (2 H, m, :CH) ($J_{F-7,H-7}$ 60, $J_{F-7,H}$ 12, $J_{F-2,H-2}$ 57 Hz), $m/e$ 130 ($M^+$, 25%), 109 (10), 97 (18), 84 (100), and 79 (65) (Found: C, 64.5; H, 6.05%; $M^+$, 130.058 9).

1,4-*Dihydro*-1,4-*methanonaphthalehene*. 2-exo,9-syn-*Difluoro*-1,4-*dihydro*-1,4-*methanonaphthalene* (7) was purified by preparative g.l.c. [SE-30, Chrom A–AW 45—60 (10%); 150 °C]; yield 52%, waxy solid, m.p. (sealed capillary) 40—43 °C, $\delta_F$ (CCl$_4$) −182.25 (m, F-2) and −183 p.p.m. (dd, F-9), $\delta_H$ 4.75 (dm, H-2), 4.7 (d, H-9), 3.7 (d, H-1), and 3.45 (H-4) $m/e$ 180 ($M^+$, 88%), 159 (47), 147 (76), 146 (62), 130 (100), 133 (89), 129 (87), 116 (50), and 115 (55) (Found: C, 73.5; H, 5.9%; $M^+$, 180.075 5. C$_{11}$H$_{10}$F$_2$ requires C, 73.3; H, 5.6%; $M$, 180.075 0).

Fluorination was repeated three times; the average dis-

for 1 h. After work-up the n.m.r. spectrum showed no significant difference.

*Hydrogenation of the Difluoronorbornene* (5).—Compound (5) (0.5 mmol) was hydrogenated in methanol (3 ml) containing palladium–carbon at room temperature. After 0.3 mmol of hydrogen had been absorbed the catalyst was filtered off and the mixture was analysed by g.l.c. The retention time of the product was identical with that of 2-*exo*,7-*syn*-difluoronorbornane.[16] The n.m.r. spectra of the two compounds were the same.