Chemistry of Organo Halogenic Molecules. Part XLVII.
Stereochemistry of Iodofluorination of 1,2– and 1,4–Dihydronaphthalene
with (Difluoroiodo)methane

Stojan Stavber and Marko Zupan

Department of Chemistry and "Jožef Stefan" Institute, University of Ljubljana,
61000 Ljubljana, Yugoslavia

Summary:

Reaction of (difluoroiodo)methane with 1,2–dihydronaphthalene resulted in the
formation of vicinal iodofluorides; the reaction follows Markovnikov type regio-
selectivity and is stereospecifically anti. Reaction with 1,4–dihydronaphthalene
also occurs stereospecifically anti, and further elimination reaction leads to
naphthalene.

Introduction

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
methods[5–8] are of particular interest for the preparation of (difluoroiodo)
arenes. The reaction of xenon difluoride with methyliodine [9] or iodoarenes[10]
resulted in the formation of difluoroiodo products, which were readily used in
further reactions. There are important differences between the reactivity of (di-
fluoroiodo)methane and (difluoroiodo)arenes with alkenes. Reaction of (difluoro-
iodo)methane with phenyl substituted alkenes resulted in the formation of
vicinal iodofluorides. The reaction followed Markovnikov type regioselectivity and
was stereospecifically anti [11,12,13]. The reaction with phenylsubstituted acetylenes
also followed Markovnikov type regioselectivity and occured stereospecifically syn.[14]
On the other hand the reaction of (difluoroiodo)arenes with phenyl substituted
olefins resulted in the formation of rearranged geminal difluorides[15], while the re-
action with norbornene[15] resulted in the formation of three products; fluoro-
nortricyclane,2–exo–7–syn–difluoronorbornane and 2–exo–7–anti–difluoronorbor-
nane, the product distribution depending upon the substituent on the phenyl ring.

Similar dependence of the product distribution was also observed in the fluori-nation reactions of norbornadiene[16] mechanism which explains the formation of vicinal iodofluorides and rearranged geminal difluorides is presented in Scheme 1.

In this report we would like to present our further investigations of the reaction of (difluoroiodo)methane with 1,2–dihydronaphthalene and 1,4–dihydro-naphthalene.
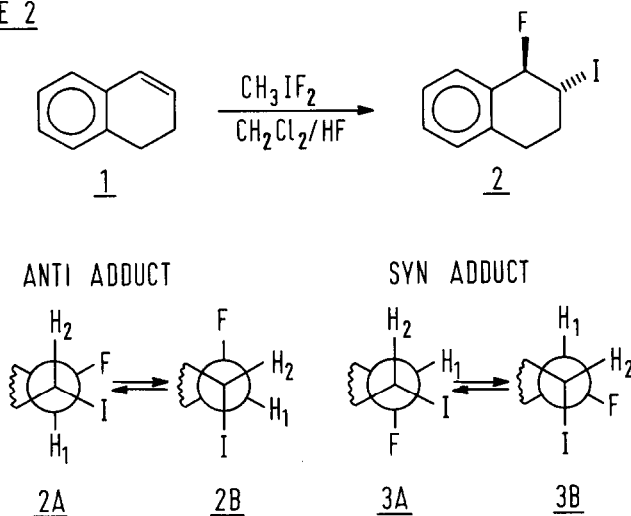
SCHEME 1
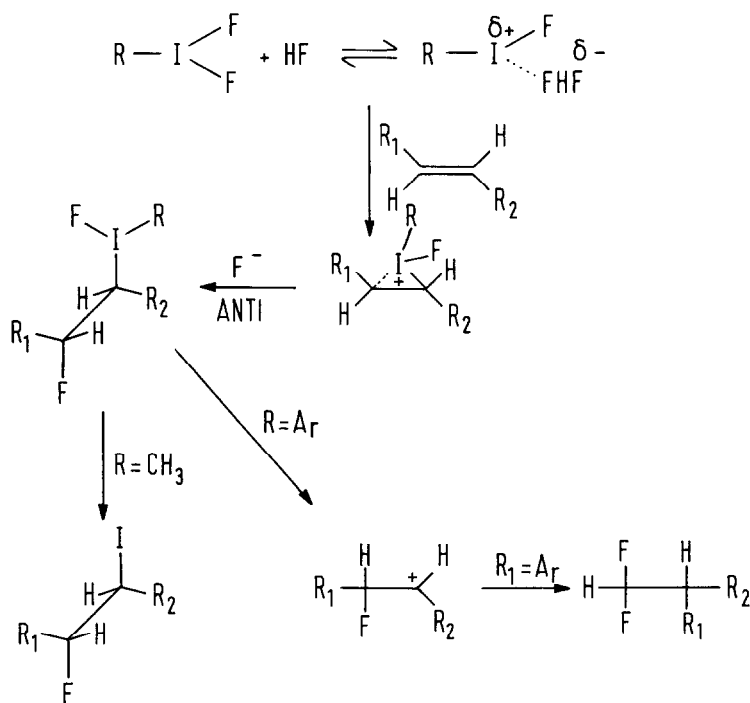
Results and discussion

The preparation of fluoroalkanes presents a different problem from that of other haloalkanes and necessitates a specific method of fluorination[17]. Difficulties involve the handling of anhydrous hydrogen fluoride on the laboratory scale and the need for pressure equipment and low temperatures, and the ease of polymerization of the starting olefines and the products. Iodofluorination with hydrogen fluoride–pyridine–N–iodosuccinimide avoids experimental difficulties[18]. Following the pro-cedure reported by Gibson[9], we prepared a solution of (difluoroiodo)methane by

the reaction of xenon difluoride with an excess of methyliodide. A 1—hour re-
action with 1,2—dihydronaphthalene(1) (Scheme 2) resulted in a crude product,
which showed in its ^{19}F nmr spectrum one doublet of multiplet signal at
δ = $-$ 139 ppm, and in its proton spectrum two signals at lower field δH_1 =
5,6 ppm (dd) and δH_2 = 4,6 ppm (m) with the following coupling constants:
$^2J_{FH_1}$ = 54 Hz, $^3J_{FH_2}$ = 9 Hz. The product was found to be stable in a 1 M
solution of potassium t—butoxide at T = 30°C. Under the mentioned conditions,
we have observed that cis—1—fluoro—2—halo—1,2,3,4—tetrahydronaphthalenes
undergo rapid elimination of HX, thus forming 1—fluoro—3,4—dihydronaphtha-
lene[19]. On the basis of the coupling constants (the Newman projections of two
possible isomers: anti adduct (2A, 2B) and syn adduct (3A, 3B) are shown in
Scheme 2) and the chemical stability under basic conditions, we have established
that trans—1—fluoro—2—iodo—1,2,3,4—tetrahydronaphthalene (2) was formed. The
reaction followed Markovnikov type regioselectivity and occurred stereospecifically
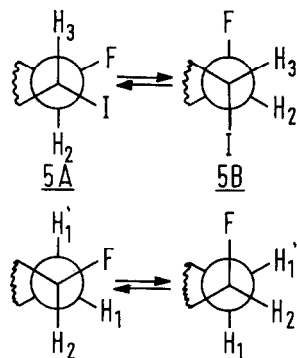anti.

SCHEME 2

ANTI ADDUCT   SYN ADDUCT

2A   2B   3A   3B

The 1—hour reaction of (difluoroiodo)methane with 1,4—dihydronaphthalene (4)
(Scheme 3) resulted in the formation of a crude product, which showed in its
[19]F nmr spectrum one signal at δ = $-$ 165 ppm (dtd) and in its ^{1}H spectrum
two signals at lower field: δH_2 = 5,0 ppm (ddd) and δH_3 = 4,5 ppm (dt) with
the following coupling constants: $^2J_{FH_2}$ = 52,5 Hz, $^3J_{FH_3}$ = 7 Hz, $^3J_{FH_1}$ =
= 26 Hz, $^3J_{FH_1'}$ = 26 Hz, $^3J_{H_2H_3}$ = 10 Hz, $^3J_{H_1H_2}$ = 5 Hz, $^3J_{H_3H_4}$ = 5 Hz.
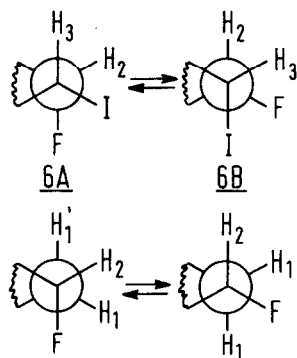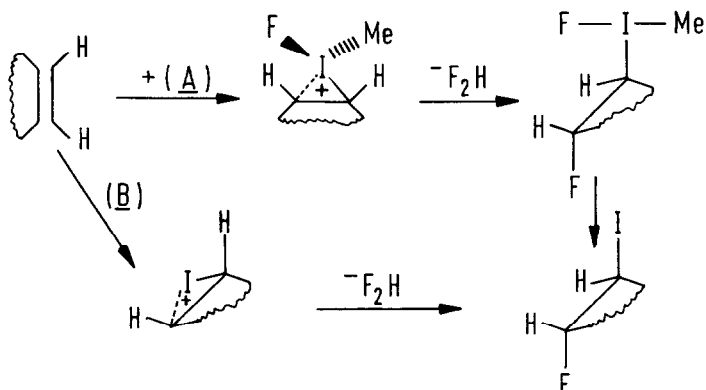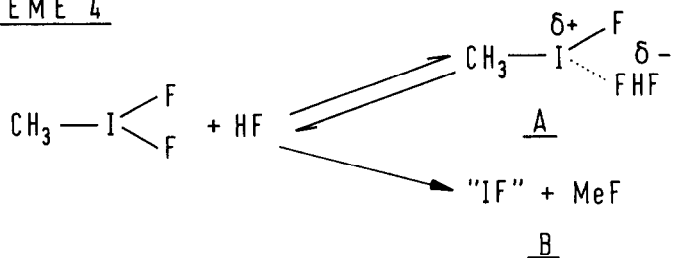
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SCHEME 3

ANTI ADDUCT   SYN ADDUCT

5A   5B   6A   6B
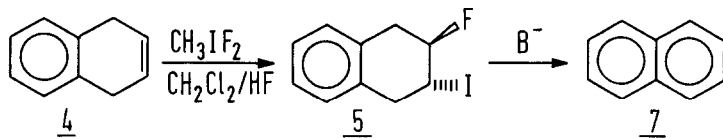
SCHEME 4

The product was found to undergo elimination under the conditions mentioned before, thus forming naphthalene (7). The Newman projections of two possible isomers (anti adduct: 5A, 5B and syn adduct: 6A, 6B) are presented in Scheme 3. On the basis of the Karplus relationship with $^3J_{FH_3}$, $^3J_{FH_1}$, $^3J_{FH_1'}$ and $^3J_{H_2H_3}$, we have established that the anti isomer was formed and that conformation 5A is more favored than 5B.

The addition of IF to olefines by (difluoroiodo)methane is in sharp contrast to the reaction of (difluoroiodo) arenes, which react with phenyl substituted olefins forming geminal difluorides with concomitant phenyl group migration. There are two possible explanations for the unusual behaviour of (difluoroiodo) methane (Scheme 4).

Either the reagent decomposes in the presence of hydrogen fluoride as catalyst to methyl fluoride and reactive species (B) which subsequently adds IF to the double bond, or the hydrogen fluoride polarizes the I−F bond of the reagent, thus forming electrophile (A), which attacks the olefinic carbon atom, methyl fluoride being eliminated in the later stage. The intermediate must be of a highly bridged nature (similar to accepted halogeno − cationic intermediates), since otherwise such high anti stereoselectivity would not be observed.

(Difluoroiodo)methane appears to be a mild selective reagent for the iodo-fluorination of olefins with stereospecific anti addition and Markovnikov type regioselectivity.

Experimental Section

I.r. spectra were recorded with a Perkin−Elmer 257 spectrometer and ^1H and ^{19}F nmr spectra with a Jeol JNM−PS−100 instrument (solvent CCl_4, Me_4Si or CCl_3F as internal reference). Mass spectra, including high resolution measurements, were taken with a CEC−21−110 spectrometer. G.l.c. was carried out on a Varian−Aerograph 1800 instrument and t.l.c. on Merck silica gel F−254.

Materials

Pure samples of 1,2−dihydro and 1,4−dihydro naphthalenes were prepared by known methods from naphthalene[20]. Methyl iodide was purified and distilled before use[21]. Hydrogen fluoride (Fluka Purum) was used. Xenon difluoride was prepared by the photosynthetic method [22] and its purity was better than 99.5 %.

Addition and Isolation Procedure

In a Kel−F vessel xenon difluoride (1,3 mmol) was dissolved in methyl iodide (2 ml) at room temperature and anhydrous hydrogen fluoride (trace) was introduced. After 20 minutes, the olefin (1 mmol) was added to the resulting brown solution of (difluoroiodo) methane and the mixture was left at room temperature for 1 hour. Methylene chloride (10 ml) was added and the solution was washed

with aqueous sodium hydrogen sulphite (10 %, 10 ml), aqueous sodium hydrogen carbonate (10 %, 10 ml) and water (10 ml), and dried (Na_2SO_4). A catalytic amount of tributylamine was added in order to prevent decomposition of the product. The solvent was evaporated off in vacuo at room temperature and the reaction mixture was analyzed by nmr and then separated by preparative t.l.c. (SiO_2, activated 2 hrs at T = 120°C, with a solution containing cyclohexane (95 %), methylene chloride (4 %) and tributylamine (1 %)).

Trans–2–fluoro–3–iodo–1,2,3,4–tetrahydronaphthalene (5)

White solid crystals, mp = 57 – 59°C, (yield 60 % from preparative t.l.c or 80 % by crystallisation from ethanol) mass spectrum: found m/e 275.9825, calcd. for $C_{10}H_{10}FI$ m/e 275.9831, m/e: 276 (M^+, 45 %), 149(80), 130(33), 129(85), 128(100), 127(35), 115(23). Nmr data: δF = 165 ppm(dtd) δH_2 = 5.0 ppm(ddd), δH_3 = 4.5 ppm(dt), $\delta H_3, H_4$ = 3–3.8 ppm(m,4H), δPh = 7.1 ppm(m,5H), $^2J_{FH_2}$ = 52.5 Hz, $^3J_{FH_3}$ = 7 Hz, $^3J_{FH_1}$ = 26 Hz, $^3J_{H_2H_3}$ = 10 Hz, $^3J_{H_1H_2}$ = 5 Hz, $^3J_{H_3H_4}$ = 5 Hz.

Trans–1–fluoro–2–iodo–1,2,3,4–tetrahydronaphthalene (2)

White crystals, the product decomposing in the pure state at room temperature. Mass spectrum: found m/e 275.9816, calcd. for $C_{10}H_{10}FI$ m/e 275.9813, m/e 276 (M^+, 28%), 149(100), 129(75), 128(81), 115(20).
Nmr spectrum: δF = –139 ppm(dd), δH_1 = 5.6 ppm(dd), δH_2 = 4.6 ppm(m), $\delta H_3 H_4$ = 2.2 – 2.8 ppm(m,4H), Ph = 7.2 ppm(m,5H), $^2J_{FH_1}$ = 54 Hz, $^3J_{FH_2}$ = 9 Hz, $^3J_{H_1H_2}$ = 4.5 Hz.
Products 2 and 5 are unstable in the pure state at room temperature and must be stored at – 20°C in the presence of catalytic amounts of tributylamine. Microanalytical data were inaccurate, with > 0.4 % deviation from calculated values.

Elimination reaction of trans–2–fluoro–3–iodo–1,2,3,4–tetrahydronaphthalene

0.5 mmol of iodofluoride (5) was stirred with potassium t–butoxide (1 M, 2.5 ml) at 50°C for 1 hour. The mixture was cooled, mixed with water (15 ml) and extracted with methylene chloride. The extract was washed with dilute acid and water, dried ($MgSO_4$), filtered and evaporated in vacuo. The residue was analysed by g.l.c. and nmr. Naphthalene, the only product formed, was isolated by g.l.c.

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