Tetrahedron Letters,Vol.23,No.10,pp 1059-1062,1982
Printed in Great Britain

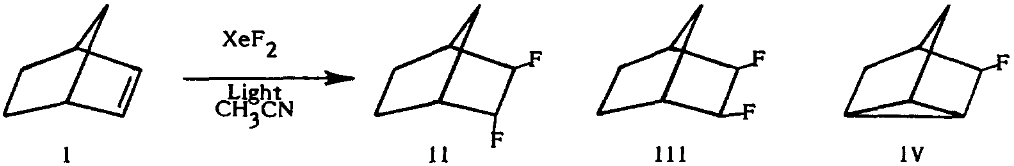
0040-4039/82/101059-04$03.00/0

XENON DIFLUORIDE FLUORINATION. IV. PHOTOCHEMICALLY INITIATED XENON DIFLUORIDE FLUORINATION OF NORBORNENE

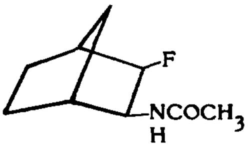
R.A. Hildreth*[1], M.L. Druelinger*[2], and S.A. Shackelford[3]
Frank J. Seiler Research Laboratory (AFSC)
USAF Academy, CO 80840

Abstract: Norbornene was selectively fluorinated with xenon difluoride by photochemical means. Unrearranged 2,3-difluoronorbornane isomers and acetonitrile solvent adducts were the exclusive products. This represents a novel example of controlled XeF_2 radical fluorination by light initiation.

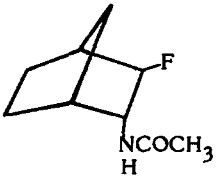
Reaction between norbornene I and xenon difluoride was achieved through photochemical initiation. Significant amounts of 2-endo-3-exo-difluoronorbornane II and 2-exo-3-exo-difluoronorbornane III formed as the sole difluoride products. This unprecedented XeF_2 photolytic fluorination represents the first selective synthesis of unrearranged 2,3-difluoronorbornane stereoisomers unique to a radical addition mechanism.[4]



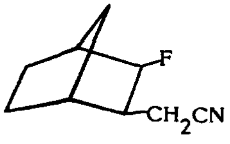
I II III IV



V



VI



VII

Furthermore, it directly complements the previously reported boron trifluoride etherate catalyzed norbornene/xenon difluoride fluorination which preferentially yields analogous 2,5-difluoronorbornane stereoisomers VIII and IX through an ionic pathway.[5,6]

Past norbornene halogenations describe a simultaneous radical/ionic mechanism. Chlorination[7] and bromination[8,9] can produce the 2-endo-3-exo- and 2-exo-3-exo-dihalonorbornanes II and III plus the respective halonortricyclane IV through a radical mechanism. However, a competing ionic mechanism concomitantly generates the syn-2,7- and some anti-2,7-dihalonorbornane[10] in addition to the halonortricyclane. This duality of mechanism is difficult to surpress and impedes the selective synthesis of halogenated stereoisomers. A similar example is reported for a hydrogen fluoride catalyzed norbornene/xenon difluoride fluorination where seven products were obtained.[11] Two minor compounds were the radically generated 2-endo-3-exo- and 2-exo-3-exo-difluoronorbornanes present in 1-11 percent and 1-6 percent product distributions, respectively. The fluoronortricyclane, common to both mechanisms, and the 2,5- and 2,7-difluoronorbornane isomer sets generated from the ionic pathway, comprised the five remaining products.[12] This photochemical xenon difluoride/norbornene fluorination exclusively provides unrearranged 2,3-difluoride and 2,3-monofluoro solvent adducts; no rearranged 2,5- and 2,7-difluoronorbornanes resulted in the light initiated reaction. The pure radical pathway represents another synthetic option to its complementary ionic reaction in which the rearranged 2,5-difluoronorbornane stereoisomers are produced by boron trifluoride etherate catalysis.

This novel photochemical fluorination was conducted in acetonitrile by irradiation with an unfiltered medium pressure Hanovia 550 watt lamp.[13] Benchtop handling techniques like those previously reported were used[14] with a Spectrosil B quartz reaction vessel[15] or normal pyrex flask. The reaction was conducted under a nitrogen atmosphere with the reaction vessel submerged in an ice/H_2O bath placed atop a cold plate stirrer. After an initial nitrogen purge, the reaction was begun at 0°C and warmed to a 7°C maximum at its termination. Table I illustrates the glpc determined product percentages achieved and the changes induced by varying either time, solvent, or reaction vessel. The 90% freon/CH_3CN solvent gave the highest yield of 2,3-difluoronorbornane isomers (51%) and surpressed the 2,3-acetoamidofluoronorbornanes (V and VI) and acetonitrile solvent adduct VII significantly[16].

TABLE I. Light Initiated XeF_2/Norbornene Fluorinated Products[17,18]

Reaction Conditions[a]	II	III	IV	V	VI	VII
(A) CH_3CN/Quartz (0.5 hr)	25	8	7	22	--[b]	29
(B) CH_3CN/Quartz (1.0 hr)	30	9	10	17	2	25
(C) CH_3CN/Pyrex (1.0 hr)	31	12	5	22	0	20
(D) 10% CH_3CN & 90% $CFCl_3$/ Quartz (1.0 hr)	40	11	7	15	2	7

a. Runs A - C percentages are based upon products only and do not include unreacted norbornene; run D includes the norbornene (ca. 9%). Other products, each less than 1%, comprise the product balances. b. Not determined. Separations were made on a 15 ft. by 3/8 in. 10% Carbowax 20M on 80/100 mesh Chromosorb W column.

Figures 1 and 2 reveal pictorial ^{1}H nmr data of the radically formed 2,3-difluoronorbornanes II and III and supplement those previously published for the 2,5-difluoronorborane isomers VIII and IX.[5]

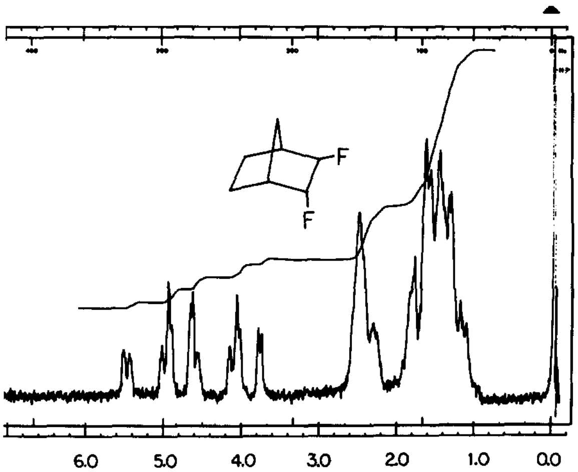


Figure 1

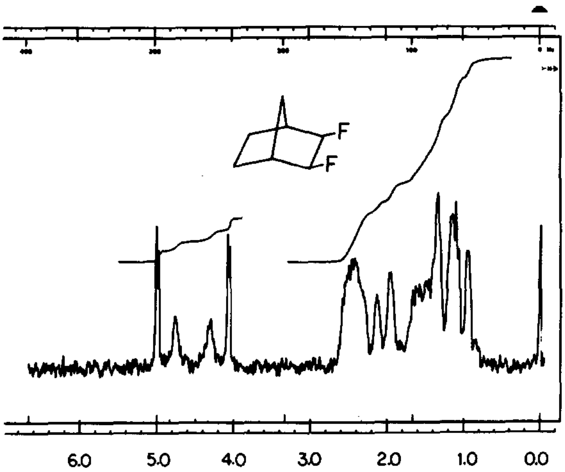
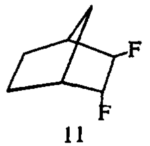


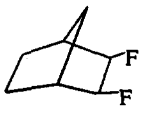
Figure 2

The striking preference of the light initiated norbornene/xenon difluoride fluorination to yield a significant percentage of the 2-exo-3-exo-difluoronorbornanes II and III as exclusive difluoride stereoisomers is a novel and useful finding. This photochemical fluorination offers an attractive alternative radical pathway to the ionic norbornene/xenon difluoride mechanism which produces the analogous 2,5-difluoronorbornanes VIII and IX. When considered separately, each mechanism with norbornene exhibits a pure, stereochemical course; but together, they supplement one another and potentially offer an advantageous system of stereochemical and mechanistic control.[19] This possibility for selective fluorine introduction into specific molecular sites by the proper choice of pure radical or ionic conditions represents an intriguing and powerful synthetic tool for application to novel or important fluoroorganic compounds; it should be investigated further.[20] A more definitive elucidation of this radical fluorination mechanism has been in progress.

radical products

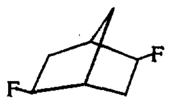


II

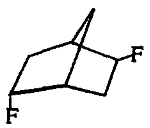


III

ionic products



VIII



IX

Acknowledgement is made to J.L. Pflug and F.C. Kibler for their extensive assistance, to B.A. Loving, J.S. Wilkes, and D.M. Lemal for constructive discussions, to A.A. Fannin for managerial support, and to Mrs. B. Hincy for typing this manuscript.

REFERENCES AND NOTES

1. Present address: AFATL/DLDE, Eglin AFB, FL 32542.
2. Present address: USAFA/DFC, USAF Academy, CO 80840.
3. Present address: AFRPL/LKLR, Edwards AFB, CA 93523.
4. R.A. Hildreth, M.L. Druelinger, and S.A. Shackelford, Fourth Winter Fluorine Conference, Daytona Beach, FL, 28 Jan - 2 Feb 1979. Preliminary results of this work were presented.
5. S.A. Shackelford, Tetrahedron Letters, 4265 (1977).
6. S.A. Shackelford, J. Org. Chem., 44, 3485 (1979).
7. M.L. Poutsma, J.Am. Chem. Soc., 87, 4293 (1965).
8. H.Kwart and L. Kaplan, J.Am. Chem. Soc., 76, 4072 (1954).
9. D.R. Marshall, P.R. Warnhoff, E.W. Warnhoff, and J.R. Robinson, Can. J. Chem., 49, 885 (1971).
10. The anti-2,7-dichloronorbornane is not reported in reference 7; minor amounts of the 2,5-dibromonorbornane isomers were also reported in reference 9.
11. M. Zupan, A.Gregorcic, and A. Pollak, J. Org. Chem., 42, 1562 (1977).
12. The probable dual mechanism is discussed in reference 11. Our photochemical study suggests the competing radical mechanism which produced II and III may have been significantly enhanced or even initiated by extraneous lighting. No similar mechanistic duality was detected in references 5 and 6.
13. A control reaction run in the dark produced no appreciable products under the conditions outlined.
14. S.A. Shackelford, R.R. McGuire, and J.L. Pflug, Tetrahedron Letters, 363 (1977).
15. Spectrosil B quartz glass gives a transmittance greater than 90% at 180 nm.
16. When CH_2Cl_2 was used as solvent, it photolyzed, and generated radical type products with Cl atom/solvent incorporation. Diethyl ether produced no fluorinated norbornanes; although, the XeF_2 immediately disappeared with rapid gas evolution upon lamp activation.
17. Compounds II, III, and IV afforded melting points, mass spectral, and/or nmr data in agreement with those reported in reference 11. Compounds V, VI, and VII were characterized by infrared, mass spectral, and nmr spectroscopy; stereochemistry was assigned based upon the large vicinal-HF ^1H nmr coupling at the bridgehead positions expected when the fluorine atom is at the exo position.
18. The stereochemical assignment of cis-2-acetoamido-3-fluoronorbornane V was further confirmed by an X-ray diffraction analysis conducted by Molecular Structure Corporation, College Station, TX 77840; N. Ely, FJSLR-TR-81-0006, Jun 1981.
19. S.A. Shackelford, R.A. Hildreth, and M.L. Druelinger, 9th International Symposium on Fluorine Chemistry, Avignon, France, 3-7 Sep 1979. "Abstracts of Papers", p. 0-36.
20. D.F. Shellhamer, R.E. Richardson, D.R. Hollingsworth, K.L. Fillmore, M. Ragains, V.L. Heasley, 1981 Pacific Conference on Chemistry and Spectroscopy, Anaheim, CA, 19-21 Oct 1981, and D.F. Shellhamer, M.L. Ragains, B.T. Gipe, V.L. Heasley, and G.E. Heasley, J. Fluorine Chem., in press. Isomers of 1-phenylpropene have been fluorinated with XeF_2 by light initiation.

(Received in USA 24 November 1981)