Tetrahedron Letters No. 41, pp 3525 - 3526, 1975. Pergamon Press. Printed in Great Britain.

STEREOCHEMISTRY OF IODOFLUORINATION OF PHENYLSUBSTITUTED OLEFINS WITH METHYLIODINE(III)DIFLUORIDE

Marko Zupan[*] and Alfred Pollak[+]
J.Stefan Institute and Department of Chemistry,
University of Ljubljana, 61000 Ljubljana, Yugoslavia

(Received in UK 22nd August, 1975; accepted for publication 29th August, 1975)

Recently, we have found that methyliodine(III) difluoride reacts with 1,1–diphenylethylenes in the presence of hydrogen fluoride as catalyst to form corresponding 1–fluoro–2-iodo-1,1–diphenylethanes[1]. We now report the results of a similar addition to cis- and trans–1–phenylpropene–1 and cis– and trans–stilbene with this reagent. The recently reported synthesis of methyliodine(III)–difluoride[2] by the reaction of xenon difluoride with an excess of methyl iodine made this potential fluorinating agent readily available. The attemped fluorination of trans–stilbene with aryliodine(III) difluorides[3] failed, but reaction with trans–1–phenylpropene–1 resulted in the rearranged product 1,1–difluoro–2–phenylpropane[4].

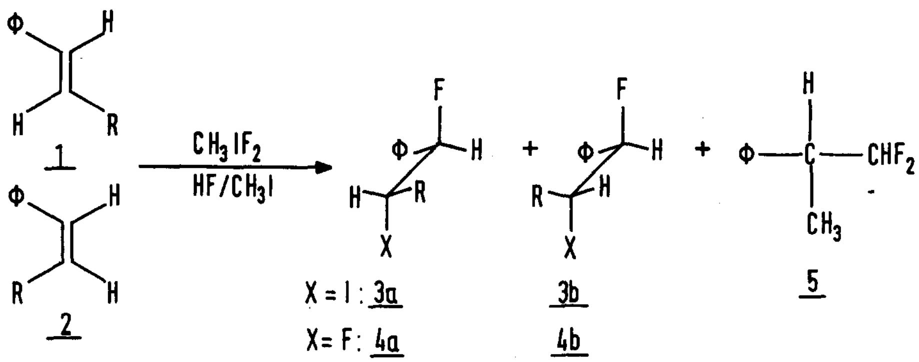
Being interested in learning whether each member of a cis and trans isomeric olefin pair would exhibit the same stereochemistry in the iodine fluoride addition with methyliodine(III)difluoride, we chose trans–(1) and cis–stilbene(2) (R = Phenyl) and 1–phenylpropene–1 (R = CH_3) for the study. In a typical experiment, anhydrous HF was introduced at 20° in 2 ml methyliodide and under stirring pure XeF_2 (1,2 mmol) was added. The solution turned dark brown and xenon gas was evolved. After 15 minutes, when gas evolution had ceased, olefin (1 mmol) was added. Two hours later the products were isolated, ^1H and ^{19}F n.m.r. spectra were taken on the crude reaction mixtures, and the products (3a), (3b), (4a), (4b) and (5) were separated by g.l.c. or t.l.c. The conversions of 1 and 2 into products were of the order of 90 %, as determined by n.m.r. or g.l.c.

The reaction of methyliodine(III)difluoride with cis– and trans stilbene gave a reaction mixture of diastereoisomeric iodofluorides (3a) and (3b) and difluorides (4a) and (4b). The product distribution data indicate that the iodofluorination of both cis– and trans– stilbene is a rather highly anti stereoselective process. The formation of difluorides exhibits lower anti stereoselectivity. The reaction with cis- and trans–1–phenylpropene–1 gave a reaction mixture of diastereoisomeric iodofluorides (3a) and (3b), trace amounts of difluorides (4a) and (4b) and about 15 % of rearranged geminal difluoride (5). As in the iodofluorination of stilbenes, a high anti stereoselectivity and exclusive Markovnikov type regioselectivity of the addition of iodine fluoride was observed.

The structures of the previously known products (4a) and (4b) were identified[5,6] and those of unknowns (3a) and (3b) assigned by their i,r, ^1H and ^{19}F n.m.r. and mass spectra, and the stereospecific anti elimination of HI affording known cis and trans phenylsubstituted fluoroolefines[6].

Isomerisation of the reacting olefins was evaluated in separate experiments stopped prior to completion. The unreacted olefin was analysed by g.l.c. Isomerisation of olefins 1 and 2 during the course of reaction is negligible. The amount of difluorides 4a and 4b or 5 is greater if a longer reaction time is used. Difluorides were formed only from olefins bearing at least one methyl or phenyl group (R)[1], which facilitates the S_N1 substitution with its mesomeric or inductive effect. Following some reactions with ^{19}F n.m.r., we observed first the formation of iodofluorides only, but in the later stages of the reactions ^{19}F peaks corresponding to vicinal or rearranged geminal difluorides appeared.

Methyliodine(III) difluoride appears to be a mild, selective agent for the iodofluorination of olefins, with some advantages in comparison to known reagents e.g. anhydrous hydrogen fluoride[7] or Olah's[8] poly–hydrogen fluoride/pyridine in connection with N–iodosuccinimide. One of them which could be mentioned here is the only catalytic amount of HF required to catalyse the reactions, which prevents the polymerisation of rather sensitive olefins or other side reactions.



RELATIVE YIELDS (%)[a]

	R	3a	3b	4a	4b	5
1	CH_3	78	4	4	–	14
	Φ	56	4	36	3	–
2	CH_3	4	80	–	1	15
	Φ	10	52	20	18	–

[a] Determined by ^{19}F n.m.r. spectroscopy

We thank Prof. J.Slivnik for the xenon difluoride, Prof. J.Marsel for providing facilities, Dr. V.Kramer for mass spectral data and Dr. J.Kobe for n.m.r. spectra.
The financial assistance of the Boris Kidrič Foundation and „Krka" – factory are acknowledged.

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[+] Present address: Dep. of Chem. Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, U.S.A.