Tetrahedron Letters,Vol.27,No.31,pp 3659-3660,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

HIGHLY REGIO- AND STEREOCONTROLLED HALOGENATION OF 1,1-DIFLUORO-2-HALO-1-ALKEN-3-OLS AS APPLIED TO POLYFLUORINATED PYRETHROID SYNTHESIS

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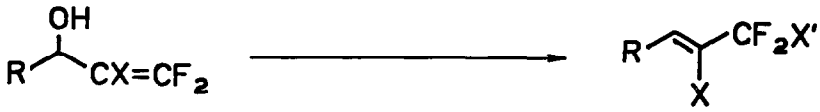
Treatment of 1,1-difluoro-2-halo-1-alken-3-ols with various halogenating reagents gave (Z)-1,1-difluoro-1,2-dihalo-2-alkenes under high regio- and stereocontrol. This transformation was applied to the construction of C-3 side chain $CH=C(X)CF_2X'$ (X, X' = F or Cl) of polyfluorinated synthetic pyrethroids.

Polyfluorovinylsilane/F^-(cat)[1] and $CCl_3CF_3/Zn/AlCl_3$(cat)[2] reagents have been revealed to provide practical methods for the introduction of $CX=CF_2$ groups (X = F, Cl) to aldehyde carbonyls. The adducts **1** are found to be successfully halogenated to give polyfluorohaloalkenes **2** under high regio- and stereocontrol. This transformation and its application to the stereocontrolled synthesis of polyfluorinated pyrethroids are described herein.



1 X = F, Cl; X' = F, Cl, Br **2**

To a dichloromethane solution of 1,1,2-trifluoro-1-tridecen-3-ol (**1a**) was added diethylaminosulfur trifluoride (DAST) (1.0 mol) at -78 °C, and the mixture was allowed to warm to room temperature over 15 min. At this time, quantitative formation of (Z)-1,1,1,2-tetrafluoro-2-tridecene (**2a**)[3] was indicated by ^{19}F NMR which also revealed no contamination by its stereo- or regioisomer. After workup, **2a** was isolated in 90% yield by preparative TLC (silica gel).

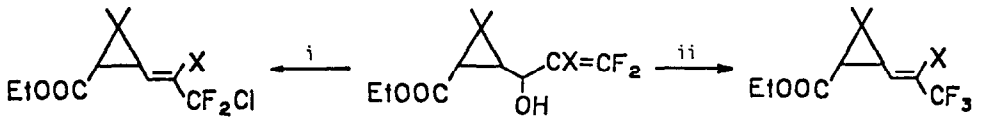
The exclusive formation of **2a** should be ascribed to high electronegativity of difluoromethylene moiety, which readily accepts nucleophilic attack by fluoride ion with concomitant deoxygenation.[5,6] The regioselective fluorination of **1** contrasts sharply to the reaction of common allylic alcohols with DAST wherein two isomeric allylic fluorides are produced in intractable ratios. Chlorination ($SOCl_2$) and bromination ($SOBr_2$) of various allylic alcohols **1**[7] also proceeded with high regio- and stereoselectivities (Table I).

Table I. Regio- and stereocontrolled halogenation of **1**

substrate (**1**)	reagent[a]/solvent	conditions	product (**2**)[b]	% yield[c]
n-$C_{10}H_{21}CH(OH)CF{=}CF_2$ (**1a**)	DAST(1.0)/CH_2Cl_2	-78 °C-rt, 0.2 h	n-$C_{10}H_{21}CH{=}C(F)CF_3$	90
1a	$SOCl_2$[e](1.0)/Et_2O	rt, 3 h	n-$C_{10}H_{21}CH{=}C(F)CF_2Cl$	85
n-$C_{10}H_{21}CH(OH)CCl{=}CF_2$ (**1b**)	DAST(1.0)/CH_2Cl_2	-78 °C-rt, 0.3 h	n-$C_{10}H_{21}CH{=}C(Cl)CF_3$	70
1b	$SOCl_2$(1.4)/Et_2O	50 °C, 13 h[d]	n-$C_{10}H_{21}CH{=}C(Cl)CF_2Cl$	90
1b	$SOBr_2$(1.2)/Et_2O	40 °C, 4 h[d]	n-$C_{10}H_{21}CH{=}C(Cl)CF_2Br$	84
c-$C_6H_{11}CH(OH)CCl{=}CF_2$	$SOCl_2$(1.0)/Et_2O	50 °C, 18 h[d]	c-$C_6H_{11}CH{=}C(Cl)CF_2Cl$	75
$PhCH(OH)CCl{=}CF_2$	$SOCl_2$(1.1)/Et_2O	50 °C, 12 h[d]	$PhCH{=}C(Cl)CF_2Cl$	79

[a]Values in the parentheses refer to mol to **1**. [b]Only (Z)-isomers were isolated. [c]Isolated yields. [d]Carried out in a sealed tube. [e]Pyridine (2.0 mol) was added.

The regio- and stereocontrolled halogenation was applied to the polyfluorinated pyrethroid synthesis. Thus, the polyfluoroallyl alcohols[9] **3a,b** were efficiently converted into **4a,b** and **5a,b**, acid parts of highly potent synthetic pyrethroids.[10]



4a	X = F, 86%	**3a**: X = F	X = F, 81%	**5a**
4b	X = Cl, 75%	**3b**: X = Cl	X = Cl, 66%	**5b**

i: $SOCl_2$(1 mol), pyridine(2 mol), Et_2O, rt, 3 h; ii: DAST(1 mol), CH_2Cl_2, -78 °C-rt, 0.3 h

References and Notes

1. M. Fujita and T. Hiyama, J. Am. Chem. Soc., **107**, 4085 (1985).
2. M. Fujita and T. Hiyama, the preceding paper.
3. The (E)-coupling constant $^3J_{H-F}$ (33 Hz) was observed. Stereochemical assignment of fluoroalkenes: S. E. Banks, "Fluorocarbon and their derivatives", MacDonald Technical Scientific (1970); p. 233.
4. (a) W. J. Middleton, J. Org. Chem., **40**, 573 (1975). (b) K. Bannai, T. Toru, T. Obi, T. Tanaka, N. Okamura, K. Watanabe, A. Azato, and S. Kurozumi, Tetrahedron, **39**, 3807 (1983).
5. W. A. Sheppard, C. M. Sharts, "Organic Fluorine Chemistry", W. A. Benjamin, Inc., New York; Chap 3 (1969).
6. Facile 1,3-rearrangement of the allylic sulfonate of **1** took place: mesylation of **1a** [MsCl/pyr., 0 °C] gave n-$C_{10}H_{21}CH{=}C(F)CF_2OSO_2Me$ as a sole product (60% yield).
7. Configuration of the products was determined by ^{19}F NMR,[3,10] or by comparison with authentic (Z)/(E) mixture.[2]
8. E. Pretsch, T. Clerc, J. Seibl, and W. Smith, "Tabellen zur Strukturaufklärung organischer Verbindungen mit spektroskopischen Methoden", Springer-Verlag, New York (1981); H-215.
9. Prepared by the fluoride ion catalyzed reaction[1] of the corresponding polyfluorovinylsilanes with ethyl 3-formyl-2,2-dimethylcyclopropanecarboxylate.
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(Received in Japan 10 May 1986)