



REGIOSELECTIVITY OF ADDITIONS OF NUCLEOPHILIC RADICALS TO FLUOROOLEFINS

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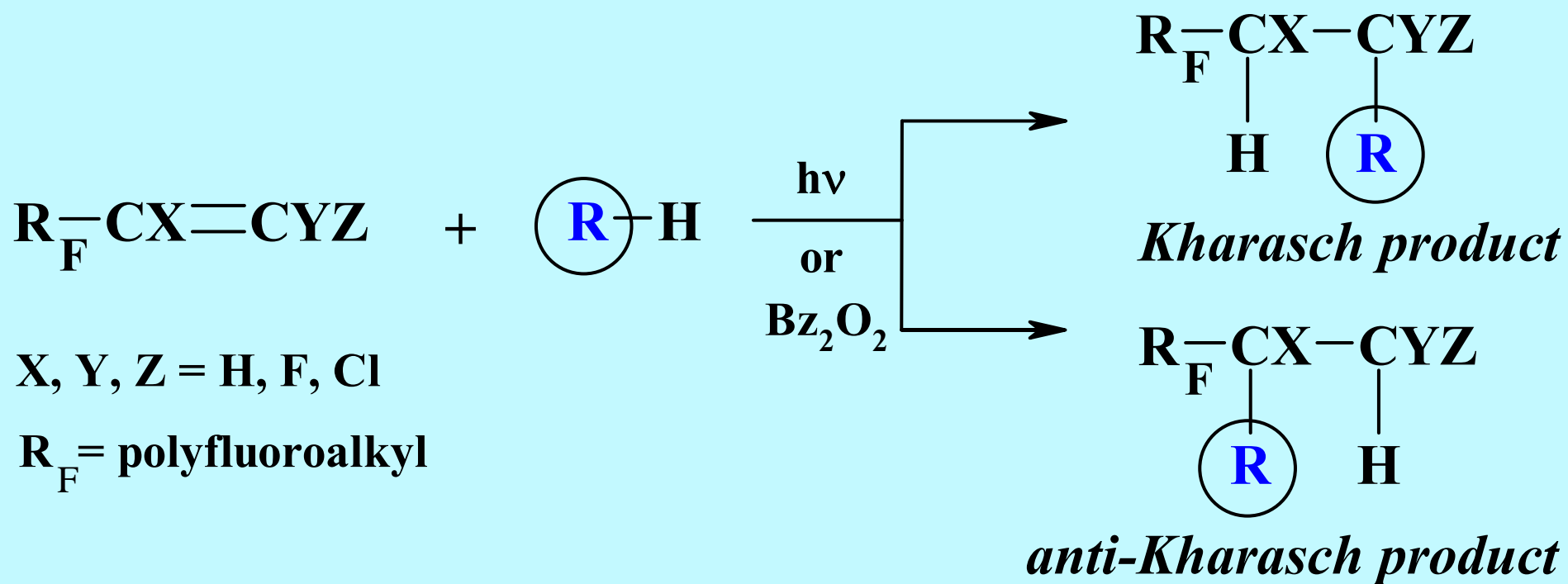
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INTRODUCTION

Radical additions to double bond of fluoroolefins are a powerful chemical tool for the formation of the new C-C bond. The reaction products can be employed as useful synthetic intermediates, special monomers and as biocompatible materials for medical applications.



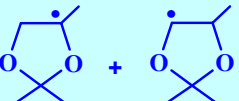
The regioselectivity of radical addition between fluoroolefins and nucleophilic radicals is strongly influenced by the Lewis acid-base character, and by steric and polar effects of radical additive. According to previous observations, a generalized scheme of the addition reactions presupposes the formation of two regioisomeric adducts: a classical *Kharasch* product and an *anti-Kharasch* product formed by the attack of radical at the internal position. Nucleophilic radicals (R·) derived from alkanols and cyclic ethers (THF, 1,3-dioxolanes) tend to add to the terminal position of fluoroolefins. This regioselectivity is probably the result of a steric effect together with favorable interactions of frontier orbitals of the reacting species.

GENERALIZED SCHEME OF THE ADDITIONS TO FLUOROOLEFINS



The aim of this study was to determine the steric and electronic effects of fluorine and chlorine substituents in fluoroolefins **on the regioselectivity** of radical additions.

INFLUENCE OF BULKINESS OF NUCLEOPHILIC RADICALS R·

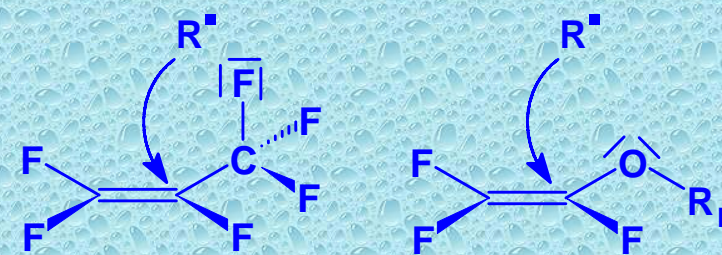
Nucleophilic radicals R·	^a CF ₂ =CF-CF ₃		^a CF ₂ =CF-O-C ₃ F ₇		^b CH ₂ =CH-C ₆ F ₁₃	
	Regioisomeric products [% rel]					
	Kharasch	anti-Kharasch	Kharasch	anti-Kharasch	Kharasch	anti-Kharasch
$\dot{\text{C}}\text{H}_2\text{OH}$	98	2	93	7	-	-
	99	1	93	7	100	0
	99	1	94	6	100	0
	87+13	0	84+12	3+1	84+16 ^c	0
$\text{CH}_3\dot{\text{C}}\text{HOH}$	100	0	96	4	100	0
$(\text{CH}_3)_2\dot{\text{C}}\text{OH}$	100	0	99	1	100	0

Initiation: ^a hv, ^b hv + acetone, ^c Bz₂O₂



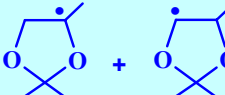
1) MOST BULKY RADICAL = SMALLER AMOUNT OF REGIOISOMER

2) STERIC REASON OF OR_F CHAIN CONFORMATION

3) COMPLETE REGIOSELECTIVITY WITH R_F-CH=CH₂



INFLUENCE OF FLUOROOLEFIN-CHAIN LENGTH OR BULKINESS

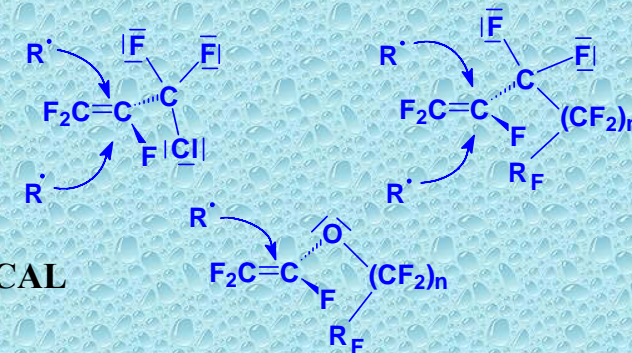
Nucleophilic radicals R·	$^a \text{CF}_2=\text{CF}-\text{C}_n\text{F}_{2n+1}$	$^a \text{CF}_2=\text{CF}-\text{CF}_2-\text{Cl}$	$^a \text{CF}_2=\text{CF}-\text{OCF}_2\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$			
	Regioisomeric products [% rel]					
	Kharasch	anti-Kharasch	Kharasch	anti-Kharasch	Kharasch	anti-Kharasch
$\dot{\text{C}}\text{H}_2\text{OH}$	100 (n=7)	0	99	1	95	5
	-	-	100	0	94	6
	100 (n=9)	0	100	0	94	6
	87+13 (n=5)	0	-	-	-	-
$\text{CH}_3\dot{\text{C}}\text{HOH}$	-	-	100	0	99	1
$(\text{CH}_3)_2\dot{\text{C}}\text{OH}$	-	-	100	0	100	0

Initiation: $^a h\nu$



1) LONGER-CHAIN FLUOROOLEFIN = SMALLER AMOUNT OF REGIOISOMER

2) CONFORMATIONAL "TAIL EFFECT" OF FLUOROCARBON CHAIN

3) "TAIL EFFECT" OF BULKY CHLORINE ATOM AND BULKY EFFECT OF RADICAL



INFLUENCE OF TERMINAL CHLORINE ATOMS

Nucleophilic radicals R·	^a Cl-CH=CF-CF ₂ Cl		^a Cl-CF=CF-CF ₂ Cl		^a CCl ₂ =CF-CF ₂ Cl	
	Regioisomeric products [% rel]					
	Kharasch	anti-Kharasch	Kharasch	anti-Kharasch	Kharasch	anti-Kharasch
	76	24	52	48	0	100
	76	24	51	49	0	100
CH₃·CHOH	86	14	73	27	0	100
(CH₃)₂·COH	97	3	95	5	0	100

^a hv; ^b 62%-E, 38%-Z; ^c 84%-E, 16%-Z

- 1) TERMINAL CHLORINE ATOMS REVERSE THE REGIOSELECTIVITY OF ADDITION OF THE NUCLEOPHILIC RADICALS
- 2) INVERSION OF REGIOSELECTIVITY IS COMBINED WITH DRAMATIC DECREASE IN THE REACTION RATE (~355 times)
- 3) STERIC HINDRANCE (H and F), ELECTRONIC REPULSION OF NON-BONDED ELECTRON PAIRS OF FLUORINE

CONCLUSION

Regioselectivity of additions of nucleophilic radicals to fluoroolefins was influenced by:

- 1) Bulkiness of nucleophilic radicals
- 2) Fluorocarbon-chain length or bulkiness
- 3) Number of chlorine atoms at the terminal position
- 4) Character of fluoroolefins; complete regioselectivity to $R_FCH=CH_2$

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