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CATALYTIC ADDITION OF TRIHALOGENOMETHANESULFENYL CHLORIDES TO OLEFINIC COMPOUNDS

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SUMMARY

Trifluoroacetic acid has been found to be an efficient catalyst for the addition of fluorochloromethanesulfenyl chlorides $CF_nCl_{3-n}SCl$ (n = 1, 2, 3) to olefins such as cyclohexene, 1-hexene, allyl bromide and vinyl bromide. The reaction with cyclohexene led to trans adducts. The addition to asymmetrical olefins afforded a mixture of Markovnikov- and anti-Markovnikov oriented adducts. The factors influencing the reaction course are discussed.

INTRODUCTION

The addition of $CF_nCl_{3-n}SCl$ **1** (n = 0 d, n = 1 c, n = 2 b, n = 3 a) to olefins has been investigated for many years. Collected literature [1, 2] cite some important examples. Petrov et al. [3] first reported the reaction of CCl_3SCl and $CFCl_2SCl$ with cyclohexene, propylene and allyl chloride. They found that these sul-

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fenyl chlorides, in contrast to non halogenated analogs, added to olefins with difficulty. Sheppard et al. [4] found that the addition of $CFCl_2SCl$ to cyclohexene took place rather smoothly in ethylene chloride at ambient temperature. Under the influence of UV-light, CF_3SCl added via a radical mechanism to numerous electron-deficient olefins, e. g. $CHF{=}CF_2$, $CFCl{=}CF_2$, $CH_2{=}CHCl$ and $CF_3CF{=}CF_2$, etc. The fact that CF_3SCl also reacted under mild conditions with some olefins, e. g. $CH_2{=}CH_2$, $CH_2{=}CHCl$ and $CHCl{=}CHCl$ etc., in a polar solvent such as tetramethylenesulfone, suggested that the ionic addition of CF_3SCl to olefins is possible. Up to now, however, no typical electrophilic addition has been reported.

RESULTS AND DISCUSSION

In the present work, we found that catalytic amounts of CF_3COOH efficiently promoted the addition of 1 to cyclohexene, 1-hexene, allyl bromide and vinyl bromide. These reactions showed typical electrophilic character in that electron-donating substituents attached to the double bond increased the reaction rate. In a like manner, the electrophility of 1, which increases with the degree of fluorination, markedly influenced the rate of addition. Thus, in the presence of CF_3COOH, the electron-abundant olefins, cyclohexene and 1-hexene, reacted vigorously and exothermally with 1 (n = 1, 2, 3). As described in two previous papers, the more reactive olefins, ethylvinylether and norbornene, reacted spontaneously with 1 even in the absence of CF_3COOH [8, 9]. Electron-withdrawing substituents attached to the double bond reduce the electron density at the reaction center thus retarding the reaction with 1. The reaction rate of allyl bromide could still be accelerated by CF_3COOH; however vinyl bromide reacted slowly only with

1 (n = 2, 3) at room temperature and methyl acrylate showed no evidence of reaction with **1** under these same conditions. As expected, CF_3SCl was most reactive in all the additions while CCl_3SCl, strikingly different from its fluorine-containing analogs, was less sensitive toward the catalysis of CF_3COOH.

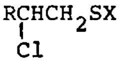
The direction and stereochemistry of these additions have been carefully considered. NMR-spectroscopy was utilized for the structural analysis and determination of isomeric ratios. The ^1H-NMR spectra of cyclohexanes **2** show the typical signals for 1,2-trans-substituted derivatives (doublet of triplets with coupling constants of 6 - 7 Hz and 3 - 4 Hz). The products obtained from the reaction of **1** with asymmetrical olefins represented a mixture of Markovnikov (M) and anti-Markovnikov (aM) adducts.

2

a b c

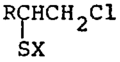
X = CF_3 CF_2Cl $CFCl_2$

M-adduct



$\underset{Cl}{RCH}CH_2SX$

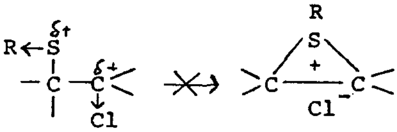
aM-adduct



$\underset{SX}{RCH}CH_2Cl$

			X =		
R =	M	aM	a	b	c
$n-C_4H_9$	3	3'	CF_3	CF_2Cl	$CFCl_2$
$BrCH_2$	4	4'	CF_3	CF_2Cl	$CFCl_2$
Br	5	5'	CF_3	CF_2Cl	

Usually, isolation of isomers obtained from non-halogenated sulfenyl chlorides and olefins is impossible owing to isomerization, i.e., a kinetically controlled aM-adduct converts readily into a thermodynamically more stable M-adduct [5]. This isomerization occurs even at ambient temperature and can be accelerated by heating or acid catalysis. However, in our investigation, we found that fluorochloromethanesulfenyl chloride-olefin adducts were sufficiently stable such that they could undergo vacuum distillation or isolation by preparative G C with no change of isomeric ratios. This unusual resistance to isomerization was due to the electron-withdrawing effect of the fluorochloromethyl group, which rendered the sulfur atom electron deficient thus making it unaccessible to attack by the ß-carbon atom. This precluded formation of a cyclic intermediate, episulfonium ion, which was necessary for the isomerization to occur [5].



A comparable effect was observed in the addition of acetylthio- and 0,0-dimethylphosphorylsulfenyl chloride to olefins which led to predominantly anti-Markovnikov adducts showing no tendency for the post-isomerization [6, 7]. Structural assignments for Markovnikov and anti-Markovnikov adducts were easily elucidated via NMR analysis. The most pure samples were obtained by preparative GC. Isomeric ratios were determined by either NMR or GC. The results are shown in Table 2. NMR data for the adducts are given in Table 4.

EXPERIMENTAL

^{1}H-NMR- and ^{19}F-NMR-spectra were obtained on a Bruker 10 P 80 S or Bruker WM 250 PFT-spectrometer. All spectra were recorded in $CDCl_3$ solution, using TMS (^{1}H) or C_6F_6 (^{19}F) [all values calibrated against $CFCl_3$] as internal standards.

$CF_nCl_{3-n}SCl$-Addition to Cyclohexene (2a, b, c, d)

$CF_nCl_{3-n}SCl$ was added slowly to a mixture of cyclohexene and trifluoroacetic acid in an exothermic reaction. Disappearance of the yellow colour of the sulfenylchloride indicated the completion of the reaction. Excess cyclohexene was removed under reduced pressure. The products were isolated by vacuum-distillation. All amounts and reaction data are given in Table 1.

$CF_nCl_{3-n}SCl$-Addition to Olefins 3, 3'; 4, 4'; 5, 5' (a, b, c)

The reaction commenced immediately as trifluoroacetic acid was added dropwise to a mixture of the olefin and the sulfenylchloride. The isomers were isolated by vacuum-distillation and separated by preparative GC. Amounts and reaction data are given in Table 2.

TABLE 1

Addition of Trihalogenomethanesulfenyl chlorides to cyclohexene (reaction data)

Reactants[a]

Cyclohexene g (mol)	Sulfenyl-chloride g (mol)	CF_3COOH [mol %[b]]	Temp. [°C]	Time [hrs]	Yield [%]	Product
27 (0.33)	1a 22.5 (0.165)	6	-20	c	95	2a
14.3 (0.174)	1b 15 (0.098)	8	0	c	93	2b
20 (0.244)	1c 28 (0.165)	7	20	c	94	2c
12 (0.146)	1d 12 (0.065)	10	20	24	80	2d

[a] An excess of cyclohexene was used . [b] Calculated on the amount of cyclohexene. [c] Instantaneous.

TABLE 2
Addition of Fluorochloromethanesulfenyl chlorides to Olefins (reaction data).

Reactants[a]							
$RCH{=}CH_2$ g (mol)	Sulfenyl chloride g(mol)	CF_3COOH [mol %[b]]	Temp. [°C]	Time [hrs]	Yield [%]	Isomer Ratio (Products) $RCHClCH_2SX$	$RCH(SX)CH_2Cl$
$R{=}n{-}C_4H_9$							
10 (0.119)	1a 14 (0.103)	7	-20	b	90	60 (3a)	40 (3'a)
6 (0.071)	1b 7.7 (0.05)	18	0	b	96	60 (3b)	40 (3'b)
4.4 (0.052)	1c 8 (0.047)	27	20	b	91	70 (3c)	30 (3'c)
$R{=}BrCH_2$							
20 (0.167)	1a 10 (0.073)	11	20	b	95	84 (4a)	14[e] (4'a)
7 (0.057)	1b 5 (0.033)	30	80	1	94[d]	87 (4b)	13[e] (4'b)
12.5 (0.104)	1c 9.2 (0.054)	17	80	2	45	87 (4c)	13[e] (4'c)
R=Br							
13 (0.121)	1a 16 (0.105)	36	20	120	88	54 (5a)	46 (5'a)
11.2 (0.105)	1b 10 (0.065)	35	20	240	50[d]	53 (5b)	47 (5'b)

[a] An excess of olefins was used. [b] Calculated on the amount of olefin.
[c] Instantaneous. [d] Conversion yield. [e] Estimated by GC.

TABLE 3
Physical and Analytical Data for $CF_nCl_{3-n}SCl$-Olefin Adducts

Product	Summary Formal of Adducts	B.p. °C (Torr)	Analysis[a], % C calcd.	found	H calcd.	found
2a	$C_7H_{10}ClF_3S$	65-66 (10)	38.44	38.5	4.58	4.7
2b	$C_7H_{10}Cl_2F_2S$	93-94 (10)	35.74	35.7	4.26	4.6
2c	$C_7H_{10}Cl_3FS$	58-59 (0.1)[b]	46.54	46.4	5.35	5.3
3a, 3'a	$C_7H_{12}ClF_3S$	43-46 (10)	38.10	38.2	5.44	5.5
3b, 3'b	$C_7H_{12}Cl_2F_2S$	77-80 (10)	35.44	35.6	5.06	5.4
3c, 3'c	$C_7H_{12}Cl_3FS$	42-45 (0.07)	33.14	33.4	4.74	5.0
4a, 4'a	$C_4H_5BrClF_3S$	53-55 (10)	18.71	18.5	1.94	2.0
4b, 4'b	$C_4H_5BrCl_2F_2S$	80-82 (10)	17.52	17.5	1.82	1.9
4c, 4'c	$C_4H_5BrCl_3FS$	108-110 (10)	16.52	16.6	1.72	1.8
5a, 5'a	$C_3H_3BrClF_3S$	35-40 (10)	14.78	14.8	1.23	1.3
5b, 5'b	$C_3H_3BrCl_2F_2S$	65-70 (10)	13.84	13.6	1.15	1.2

[a] The samples were purified primarily by vacuum distillation.
[b] 115°C (3mm) [3].

TABLE 4
NMR Spectral Data of $CF_nCl_{3-n}SCl$-Olefin-Adducts.

Compound	^{1}H chemical shifts (ppm)	^{19}F (ppm)
2a	1.25-2.65 (m, 8H), 3.46 (dt, J 6.8 and 3.7 Hz, 1H), 4.10 (dt, J 6.6 and 3.4 Hz, 1H)	40.6
2b	1.2-2.7 (m, 8H), 3.54 (dt, J 7.0 and 3.5 Hz, 1H), 4.18 (dt, J 6.0 and 3.5 Hz, 1H)	26.0
2c	1.2-2.7 (m, 8H), 3.60 (dd, J 5.8 and 5.0 Hz, 1H), 4.28 (dt, J 6.0 and 3.5 Hz, 1H)	17.5
2d	1.2-2.8 (m, 8H), 3.65 (dd, J 5.5 and 5.0 Hz, 1H), 4.50 (dd, J 4.5 and 3.5 Hz, 1H)	---
3a	0.93 (t, J 7.1 Hz, 3H), 1.25-2.05 (m, 6H), 3.21 (m, 2H), 4.04 (m, 1H)	40.5
3'a	0.93 (t, J 7.1 Hz, 3H), 1.25-2.05 (m, 6H), 3.65 (dd, J 8.1 and 3.1 Hz, 1H), 3.87 (dd, J 7.4, 3.9 Hz, 1H)	42.0
3b	0.94 (t, 3H), 1.25-1.62 (m, 4H), 1.72 (m, 1H), 1.92 (m, 1H), 3.28 (m, 2H), 4.08 (m, 1H)	25.7
3'b	0.94 (6, 3H), 1.38 (m, 3H), 1.50 (m 1H), 1.62 (m, 1H), 1.97 (m, 1H), 3.44 (m, 1H), 3.66 (dd, 1H), 3.90 (dd, 1H)	27.1
3c	0.94 (t, 3H), 1.25-2.05 (m, 6H), 3.37 (m, 2H), 4.25 (m, 1H)	17.0
3'c	0.94 (t, 3H), 1.25-2.05 (m, 6H), 3.52 (m, 1H), 3.70 (dd, J 8.1, 3.1 Hz, 1H), 3.95 (dd, J 7.6, 3.5 Hz, 1H)	19.4
4a	3.76 (m, 2H), 3.93 (m, 2H), 4.07 (m, 1H)	40.5
4b	3.80 (m, 2H), 3.90 (m, 2H), 4.13 (m, 1H)	26.0
4c	3.80 (m, 2H), 3.95 (m, 2H), 4.12 (m, 1H)	18.4
5a	3.70 (d, J 6.5 Hz, 2H), 5.80 (t, J 6.5 Hz, 1H)	42.0
5'a	4.04 (d, J 6.2 Hz, 2H), 5.40 (t, J 6.2 Hz, 1H)	42.0
5b	3.75 (d, J 6.0 Hz, 2H), 5.84 (t, J 6.0 Hz, 1H)	27.2
5'b	4.02 (d, J 6.5 Hz, 2H), 5.45 (t, J 6.5 Hz, 1H)	28.5

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