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PRELIMINARY NOTE

Reaction of Bistrifluoromethylaminosulphenyl Chloride with Fluoro-olefins and Hexafluorobut-2-yne under Free-radical Conditions

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SUMMARY

Reaction of bistrifluoromethylaminosulphenyl chloride with unsymmetrical fluoro-olefins in daylight or under photochemical conditions gives both possible 1:1 adducts (*ca*. 1:1 ratio) arising from homolytic fission of the S-Cl bond. Addition to octafluorobut-2-ene and hexafluorobut-2-yne gives mixtures of the *syn*- and *anti*- adducts.

The reaction of bistrifluoromethylaminosulphenyl chloride $(CF_3)_2NSCl$ (I) with ethylene at 70 °C did not result in 1:1 adduct formation but gave the compounds $[(CF_3)_2N]_2S$ (II), $(CF_3)_2NH$, $CF_3N{=}CF_2$, SiF_4 and $(ClCH_2CH_2)_2S$ [1]. However, treatment of a series of hydrocarbon olefins with the sulphenyl chloride (I) at -78 °C in the dark (ionic conditions) resulted in the formation of 1:1 adducts in high yield and it was

TABLE

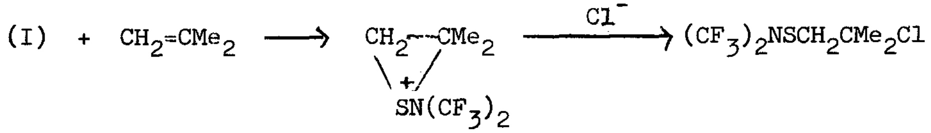
Reaction of the sulphenyl chloride (I) with fluoro-olefins, tetrachloroethene and hexafluorobut-2-yne

Alkene or alkyne (g, mmole)	(I) (g, mmole)	Conditions	Products (% yield)
CH_2=CHF (0.60, 13.50)	(2.31, 10.52)	u.v., 22 h	$(CF_3)_2NSCH_2CHFCl$ 26, $(CF_3)_2NSCHFCH_2Cl$ 25, (II) 16, (III) 3, (IV) 1, (Va) 8, (VIa) 1
CH_2=CF_2 (0.56, 8.75)	(1.82, 8.29)	u.v. 21 h	$(CF_3)_2NSCH_2CF_2Cl$ 36, $(CF_3)_2NSCF_2CH_2Cl$ 38, (II) 13, (III) 8, (Vb) 23, (VIb) 5,
CHF=CF_2 (0.91, 11.0)	(2.46, 11.21)	light, 4 d	$(CF_3)_2NSCF_2CHFCl$ 35, $(CF_3)_2NSCHFCF_2Cl$ 26, (II) 1, (III) 10.5, (Vc) 40, (VIIa) 1.5, (VIIb) 1.5, (VIII) 3.5
CF_2CFCl* (1.19, 10.19)	(2.16, 9.84)	light, 22 d	$(CF_3)_2NSCF_2CFCl_2$ 31, $(CF_3)_2NSCFClCF_2Cl$ 31, (I) 2, (II), 15, (III) 10.5 (Vd) 16, (VIc) 4, (IX) 6.5, (X) 11

$CF_2=CFCl^*$ (1.50, 12.87)	(1.80, 8.20)	u.v., 22 h	$(CF_3)_2NSCF_2CFCl_2$ 26, $(CF_3)_2NSCFClCF_2Cl$ 26, (II) 11.5, (III) 12, (IV) 3, (Vd) 11, (VIIc) 3, (XI) 3.5, (XII) 1
$CF_2=CHCF_3$ (1.75, 13.26)	(2.53, 11.53)	u.v., 30 h	$(CF_3)_2NSCH(CF_3)CF_2Cl$ 35, $(CF_3)_2NSCF_2CHClCF_3$ 22, (I) 1, (II) 11, (III) 7, (Ve) 7, (XIII) 3
$CF_2=CFCF_3{}^*$ (1.11, 7.40)	(1.91, 8.70)	u.v., 21 h	$(CF_3)_2NSCF_2CFClCF_3$ 33, $(CF_3)_2NSCF(CF_3)CF_2Cl$ 33, (I) 9, (II) 20, (III) 10, (Vf) 3
$CF_3CF=CFCF_3{}^‡$ (0.98, 4.90)	(0.86, 3.92)	u.v., 21 h	$(CF_3)_2NSCF(CF_3)CFClCF_3$ 59,† (II) 8, (III) 22, (IV) 11, (Vg) 36, (VIId) 5
$CCl_2=CCl_2$ (2.53, 15.24)	(3.33, 15.17)	u.v., 21 h	$(CF_3)_2NSCCl_2CCl_3$ 32, (II) 15, (III) 48, (Vh) 9.5, (VIIe) 3
$CF_3C\equiv CCF_3$ (1.16, 7.17)	(1.58, 7.20)	light, 7 d	(E)-$(CF_3)_2NSC(CF_3)=CClCF_3$ 42 (Z)-$(CF_3)_2NSC(CF_3)=CClCF_3$ 21, (II) 4, (III) 10.5, (XIV) 11, (XV) 4, (XVI) 2, (XVII) 10, (XVIII) 4.5

All reactions were carried out *in vacuo* in sealed Pyrex ampoules. * 1:1 Adducts could not be separated by g.l.c. † Mixture of *erythro*- and *threo*- adducts (1:1 ratio). ‡ Mixture of *cis*- and *trans*- isomers (1:3 ratio).

considered that these products probably arose via cyclic sulphonium or chloronium ion intermediates [2], e.g.



In the present work the sulphenyl chloride (I) was prepared by treatment of the mercurial $[(CF_3)_2N]_2Hg$ with sulphur dichloride [3] and its reaction with various fluoro-olefins, tetrachloroethene, and hexafluorobut-2-yne was investigated; the results obtained are summarised in the Table.

Although the 1:1 adduct yields were reasonable they were lower than those obtained from the ionic additions to hydrocarbon olefins [2] because of byproduct formation. The results obtained with octafluorobut-2-ene and hexafluorobut-2-yne show conclusively that the adducts are formed by a radical pathway and not by a concerted syn-addition of the sulphenyl chloride (I) via a four-centre transition state.

Radical attack on the olefin CF_2=CFCl is known to take place almost exclusively on the CF_2 group {the addition of CF_3I to this olefin affords a small proportion (1%) of the adduct $CF_3CFClCF_2I$ formed via $CF_3\cdot$ radical attack on the CFCl group [4]} and so it is apparent that both the $(CF_3)_2NS\cdot$ radical and the chlorine atom initially attack the olefin {cf. radical addition of the sulphenyl chloride CF_3SCl to fluoro-olefins [5]}. The results obtained from the addition of (I) to the other fluoro-olefins are consistent with this.

An interesting observation was that although the olefin dichloride (V) was formed in each reaction a compound of type $(CF_3)_2NS\overset{|}{\underset{|}{C}}\overset{|}{\underset{|}{C}}SN(CF_3)_2$ was not detected in any of the reactions.

$[(CF_3)_2N]_2S_x$

(III) x=2

(IV) x=3

$ClCWXCYZCl$

(V)

a; W=X=Y=H, Z=F

b; W=X=H, Y=Z=F

c; W=H, X=Y=Z=F

d; W=X=Y=F, Z=Cl

e; W=X=F, Y=H, Z=CF_3

f; W=X=Y=F, Z=CF_3

g; W=Y=F, X=Z=CF_3

h; W=X=Y=Z=Cl

$(CF_3)_2NCWXCYZSN(CF_3)_2$

(VI)

a; W=X=Y=H, Z=F

b; W=X=H, Y=Z=F

c; W=X=Y=F, Z=Cl

$(CF_3)_2NSSCWXCYZCl$

(VII)

a; W=H, X=Y=Z=F

b; W=X=Y=F, Z=H

c; W=Y=Z=F, X=Cl

d; W=Y=F, X=Z=CF_3

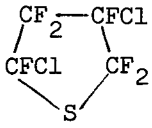
e; W=X=Y=Z=Cl

$(CF_3)_2NS(C_2HF_3)_2Cl$

(VIII)

$CF_2ClCFClCF_2CFCl_2$

(IX)



(X)

$(CF_3)_2NS(C_2F_3Cl)_2Cl$

(XI)

$(CF_3)_2NSS(C_2F_3Cl)_2Cl$

(XII)

$(CF_3)_2NS(S(C_3HF_5)_2Cl$

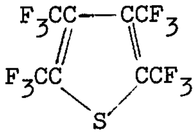
(XIII)

$CF_3CCl{=}CClCF_3$

(XIV)

$[CF_3CCl{=}C(CF_3)]_2$

(XV)



(XVI)

$(CF_3)_2NSSC(CF_3){=}CClCF_3$

(XVII)

$[CF_3CCl{=}C(CF_3)]_2S$ (XVIII)

The isolated individual 1:1 adducts (or mixtures of 1:1 adducts as indicated in the Table) possessed correct elemental compositions and their structures were established spectroscopically [i.r., n.m.r. (^{1}H and ^{19}F) and mass].

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