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REACTIONS OF IMIDOBIS(SULFURYL FLUORIDE) AND N-CHLOROIMIDOBIS(SULFURYL FLUORIDE) WITH OLEFINS.

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SUMMARY

Reactions of $HN(SO_2F)_2$ and $ClN(SO_2F)_2$ with cis-and trans-$(CH_3)CH{=}CH(CH_3)$, $H_2C{=}CF_2$, and cis CHF=CHF have been studied. The addition of $ClN(SO_2F)_2$ with cis-and trans-$(CH_3)CH{=}CH(CH_3)$ is stereospecific and trans while the addition to cis-CHF=CHF is non-stereospecific. Addition of $HN(SO_2F)_2$ follows Markownikoff's rule and $ClN(SO_2F)_2$ addition always places the $N(SO_2F)_2$ group on the most positive carbon. ^1H, ^{19}F nmr and infrared spectroscopy and mass spectrometry have been used to characterize the adducts.

INTRODUCTION

The chemistry of imiodobis(sulfuryl fluoride), $HN(SO_2F)_2$, and its derivatives has not been studied extensively. Imidobis(sulfuryl fluoride) is a relatively strong acid in aqueous medium (1). It reacts with alkali metal carbonates (1) to give $MN(SO_2F)_2$[M=K, Rb and Cs]. Fluorination of $HN(SO_2F)_2$ at ambient temperature gives $FN(SO_2F)_2$ (2). Reaction of the acid with silver oxide in trifluoroacetic acid gives $AgN(SO_2F)_2$ which reacts with alkyl halides (1) to give $RN(SO_2F)_2$ (R=Et,Me), and with $Mn(CO)_5Br$ in CH_2Cl_2(3) to give $Mn(CO)_5N(SO_2F)_2$. $MeN(SO_2F)_2$ reacts as a methylating agent towards amines and phosphines (1). No reactions of $HN(SO_2F)_2$ with olefins have been reported. N-chloroimidobis(sulfuryl fluoride) has been prepared by the reaction of $AgN(SO_2F)_2$ with Cl_2 (4). Photolysis of $ClN(SO_2F)_2$ produces $N_2(SO_2F)_4$ in high yield (4). $ClN(SO_2F)_2$ undergoes addition reactions when heated with CO, ClCN, and BrCN (4). The addition of

$ClN(SO_2F)_2$ to C_3F_6 has been reported (5) although little information concerning the mechanism of addition to olefins is available. This paper describes our investigation of the addition reactions of both $HN(SO_2F)_2$ and $ClN(SO_2F)_2$ to olefins and proposes a mechanism for the addition of $ClN(SO_2F)_2$.

EXPERIMENTAL

Standard vacuum line techniques were employed to handle all volatile compounds. Solids and non-volatile liquids were handled under nitrogen in a dry bag. IR spectra of all compounds were recorded on Perkin-Elmer Model 580 spectrophotometer either as neat liquids or in the gas phase using silver chloride windows. ^1H and ^{19}F nmr spectra were recorded at 90 MHz and 84.0 MHz respectively on a Varian Model EM-390. Mass spectra were recorded on a Dupont 491 double focusing mass spectrometer equipped with a Finnigan Incos Data System. Samples were injected as liquids. Fluoro-olefins and butenes were used without further purification. However, their purity was checked by IR spectra and also by vapor phase chromatography. Imidobis(sulfuryl fluoride) (6) and N-chloroimidobis(sulfuryl fluoride) (4) were prepared as reported in literature.

Preparation of Adducts

(i) Adducts of $ClN(SO_2F)_2$ with $CH_2{=}CF_2$, CHF=CHF and cis- and trans- $(CH_3)CH{=}CH(CH_3)$: A known weight (3-5 mmol) of $ClN(SO_2F)_2$ was condensed into a pressure reactor fitted with Fisher-Porter valves. A slight excess (than required for 1:1 mole ratio) of fluoro-olefin or olefin was condensed in the reactor at -196°. The contents were then slowly allowed to come to room temperature. Reactions were usually complete within a few hours at room temperature. After the reaction was over excess olefin was removed and the non-volatile liquid product was pumped to a constant weight.

(ii) Adducts of $HN(SO_2F)_2$ with fluoro-olefins: A known weight (10-15 mmol) of $HN(SO_2F)_2$ was transferred under N_2 in a glove bag, to the reactor as described above. A slight excess (than required for 1:1 mole ratio) of fluoro-olefin was condensed into the reactor at -196°. The reactants were allowed to come to room temperature and then heated in an oil bath at 60-70° for 4-5 hours. A colorless water-like liquid (less viscous than acid) was formed. After the completion of the reaction, excess of fluoro-olefin was pumped off and the water-like nonvolatile liquid was pumped to a constant weight.

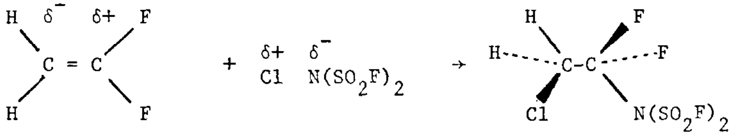
(iii) Adducts of $HN(SO_2F)_2$ with cis- and trans-2-butene; A known weight (10-15 mmol) of $HN(SO_2F)_2$ was transferred to the reactor as described above. About 30 ml of distilled and dry $CHCl_3$ was also transferred to the reactor. A slight excess (than required for 1:1 mole ratio) of butene was condensed in the reactor at -196°. The contents were allowed to come to room temperature and magnetically stirred for ∿12 hours. Excess unreacted butene and chloroform were removed in vacuo. A colorless non-volatile viscous liquid obtained was pumped to a constant weight.

RESULTS and DISCUSSION

Imidobis(sulfuryl fluoride), $HN(SO_2F)_2$ reacts with the olefins in a manner which parallels that of HF addition. Hydrogen fluoride adds to olefins obeying Markownikoff's rule or it may induce polymerization of the olefin (7). In the case of halogenated olefins, the polymerization tendency decreases with an increasing number of halogen atoms directly bonded to the sp^2 hybridized carbons of the olefin (7). Similarly $HN(SO_2F)_2$ reacts with 1,1-difluoroethylene to give $CH_3CF_2N(SO_2F)_2$ according to Markownikoff's rule. The ^1H nmr (Table 1) and ^{19}F nmr (Table II) clearly indicate the mode of addition. The ^1H nmr contains a triplet ($^3J_{H-F}$=15.9 Hz) centered at -2.19 ppm from $(CH_3)_4Si$. The ^{19}F nmr spectrum relative to CCl_3F contains a triplet at -61.9 ppm ($^4J_{F-F}$=9.3 Hz) due to the SO_2F groups and a triplet of quartets ($^3J_{H-F}$=15.6, $^4J_{F-F}$ = 9.3 Hz) due to the CF_2 group. Very little polymerization of the olefin was observed. Reaction of cis- or trans-2-butene with $HN(SO_2F)_2$ at 80° gave $CH_3CH_2CH(CH_3)N(SO_2F)_2$ although some polymerization of the olefin was observed. Both $N(SO_2F)_2$ adducts are isolated as colorless liquids.

No addition was observed when $HN(SO_2F)_2$ and cis-CHF=CHF were reacted even when the reaction mixture was heated to 80-90° for 12-14 hours. Again this follows the pattern of HF addition to olefins since HF fails to add to halogen containing olefins such as CHCl=CHCl even under drastic conditions (8,9).

Reactions of the olefins with $ClN(SO_2F)_2$ seems to parallel the reactions of olefins with halogens or interhalogens (10,11). With $CH_2=CF_2$, $ClN(SO_2F)_2$ reacts to give $CH_2ClCF_2N(SO_2F)_2$ in high yield in accordance with the postulated mechanism for the addition to C_3F_6 (5).



The ^1H nmr (Table I) and ^{19}F nmr (Table II) spectra allow unequivocal assignment of the mode of addition. The ^1H nmr appears as a triplet ($^3J_{H-F}$=15.0 Hz) centered at -4.16 ppm from $(CH_3)_4Si$. The ^{19}F nmr contains two resonances centered at -63.0 ppm and + 75.5 ppm relative to CCl_3F. The former resonance appears as a triplet ($^4J_{F-F}$, 9.6 Hz) and is assigned to the SO_2F group while the latter (assigned to CF_2 group) appears as a triplet ($^3J_{H-F}$ =15 Hz) of triplets ($^4J_{F-F'}$ = 9.6 Hz)

In contrast to $HN(SO_2F)_2$, $ClN(SO_2F)_2$ adds to cis-CHF=CHF to give the adduct as a colorless liquid in high yield. Interpretation of the ^1H and ^{19}F nmr is complicated by the presence of two chiral centers and by the fact that the molecule is an AXBX' spin system further complicated by a first order perturbation by the fluorine of the SO_2F group. However, the SO_2F region can only be interpreted in terms of more than one $N(SO_2F)_2$ group since the ^{19}F nmr spectrum in the SO_2F region indicates at least four different SO_2F resonances (Table II) thereby suggesting that the addition is not stereospecific. The addition of $ClN(SO_2F)_2$ parallels the addition of halogens to fluorinated olefins which are known to be non-stereospecific.

TABLE I

^{1}H NMR of Olefin Adducts of $ClN(SO_2F)_2$[1]

Compound	CH_3	CH_2	CH	Coupling Constants, Hz
$CH_3CF_2N(SO_2F)_2$	-2.19t			$^3J_{F-H}$ 15.9
$CH_2ClCF_2N(SO_2F)_2$		-4.6t		$^3J_{F-H}$, 15.0
$CH_3CH_2CH(CH_3)N(SO_2F)_2$[2]	-1.03t	-1.09m	-4.53	$^3J_{H_A-H_B}$, 6.0
				$^3J_{H_B-H_C}$, 6.0
				$^3J_{H_C-H_D}$, 6.0
$CH(CH_3)ClCH(CH_3)N(SO_2F)_2$[3]	-1.70d		-4.53m	$^3J_{CH_{3A}-H_B}$, 6.0
	-1.56d			$^3J_{CH_{3D}-H_C}$, 5.4
$CH(CH_3)ClCH(CH_3)N(SO_2F)_2$[4]	-1.80		-4.35	$^3J_{CH_{3A}-H_B}$, 7.0
	-1.45			$^3J_{CH_{3D}-H_C}$, 7.0

1. ^{1}H NMR shifts in ppm relative to $(CH_3)_4$ Si. d=doublet, t=triplet, m=multiplet.
2. Assignments based on $(CH_3)^ACH_2{}^BCH^C(CH_3)^DN(SO_2F)_2$.
3. From cis-2-butene, assignments based on $(CH_3)^ACH^BClCH^C(CH_3)^DN(SO_2F)_2$
4. From trans-2-butene, assignments based on same designation as cis- product.

Addition of $ClN(SO_2F)_2$ to cis- or trans-2-butene is particularly interesting since different isomers are observed depending on the starting olefin. While only one relatively broad $N(SO_2F)_2$ group is observed in the ^{19}F nmr spectrum (-59.0 ppm from CCl_3F), the ^{1}H spectrum of the cis-adduct is clearly different from that of the trans-adduct (Figure I). Although an absolute identification of the isomers was not made, there can be no doubt that the addition is stereo-

TABLE II

^{19}F NMR of Products of Olefins with $ClN(SO_2F)_2$ and $HN(SO_2F)_2$*

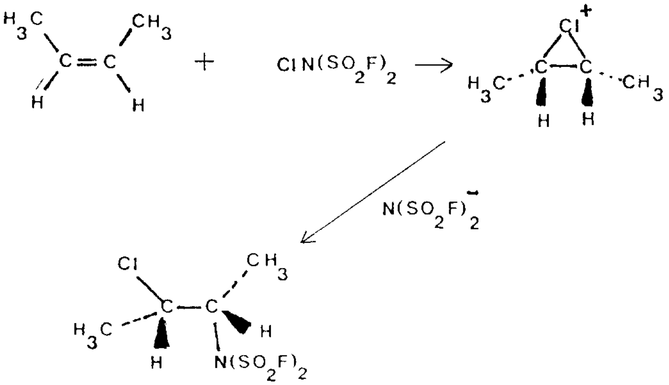
Compound	δ (CF)	δ (SO_2F)	Coupling Constants, Hz
$CH_3CF_2N(SO_2F)_2$	+63.0tq	-61.9t	$^4J_{FF}$, 9.3 $^3J_{HF}$, 15.6
$ClCH_2CF_2N(SO_2F)_2$	+75.5tt	-63.0	$^4J_{FF}$, 9.6 $^3J_{H-F}$, 15.0
$ClCHFCHFN(SO_2F)_2$	+133.5cm	-53.9cm	
	+144.0cm	-54.8cm	
	+147.0cm	-59.5cm	
	+154.2cm	-60.8cm	
$C_4H_9N(SO_2F)_2$		-59.2s	
$ClCH(CH_3)C(CH_3)H[N(SO_2F)_2]$**		-59.0s	

*Chemical shifts in ppm relative to CCl_3F. t=triplet, q=quartet, s=singlet, cm= complex multiplet.

**Same chemical shift for both cis-and trans-addition products.

specific. We suggest that addition takes place through a bridged intermediate similar to halogen addition to olefins followed by trans- attack of the $N(SO_2F)_2$ via the following mechanism.

(a)



threo isomer

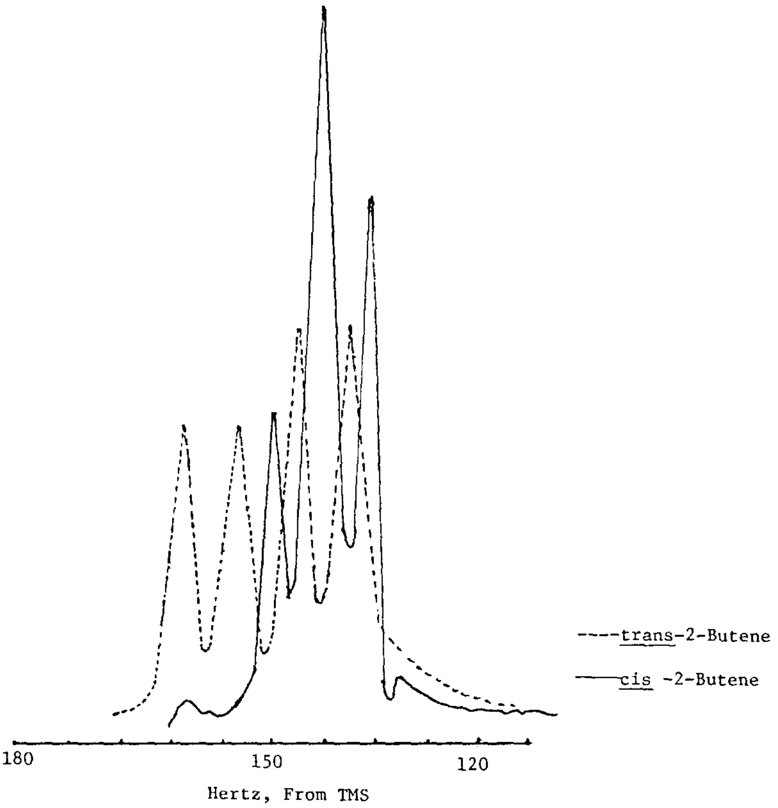
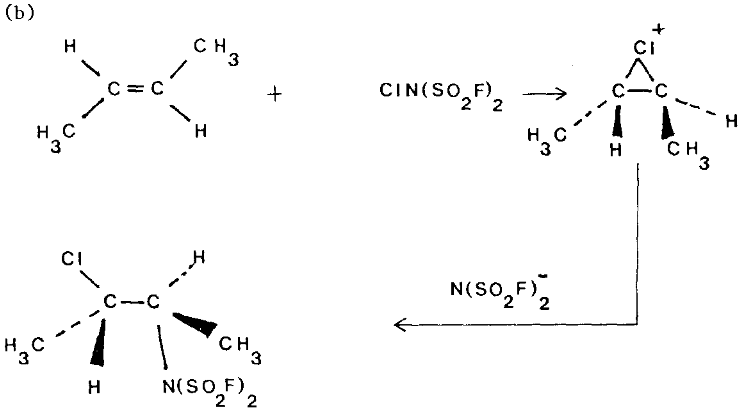


Fig. I. ^{1}H NMR Spectrum of Adducts of *cis*- and *trans*-2Butene with $ClN(SO_2F)_2$ in the Methyl Region.

(b)



erythro isomer

The important infrared bands of various adducts along with those of $HN(SO_2F)_2$ and $ClN(SO_2F)_2$ are listed in Table III. The IR spectrum of $S_2O_5F_2$ is also included for comparison. The similarity in the IR spectrum of $HN(SO_2F)_2$ and $ClN(SO_2F)_2$ with that of $S_2O_5F_2$ suggests that there are two equivalent SO_2F groups in these molecules. This fact is further supported from a single peak in their ^{19}F nmr, i.e., $HN(SO_2F)_2$ at -58.5 ppm (6) and $ClN(SO_2F)_2$ at -57.9 ppm (4). A band at 3320 in $HN(SO_2F)_2$ is attributed to ν N-H. The broad nature of the band may be attributed to the strong intramolecular hydrogen bonding in the pure acid. In its adducts with olefins (Table III) this band disappears. In the adducts of $HN(SO_2F)_2$ with butenes, the bands at 2900-2980 cm^{-1} (not shown in the table may be assigned to ν C-H. Very strong bands at 1470 and 1220 cm^{-1} in $HN(SO_2F)_2$ are assigned to ν_{asy} S-O and ν_{sym}S-O modes respectively. The strong bands at 923 and 832 cm^{-1} are assigned to ν S-N and ν S-F respectively. The bands due to ν_{asy} and ν_{sym}S-O in $ClN(SO_2F)_2$ appear at 1495 and 1231 cm^{-1} respectively, while ν S-N and ν S-F appear at 904 and 849 cm^{-1} respectively. In the adducts the bands due to ν_{asy} S-O ν_{sym} S-O ν S-F and ν S-F appear almost in the same range. The infrared spectral data for the adducts of $ClN(SO_2F)_2$ with $CH_2{:}CF_2$ and CHF:CHF are consistent with that of similar adducts of C_3F_6 with $ClN(SO_2F)_2$ (5).

The mass spectra of the adducts were recorded (Table IV). In general no parent ion could be observed but the fragmentation pattern is certainly consistent with the assigned structures. Loss of alkyl or haloalkyl groups produced the ions of highest mass. Further fragmentation of the parent by loss of the $N(SO_2F)_2$ group or $HN(SO_2F)_2$ was generally observed.

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TABLE III

IR Spectral Data[a]

Compound	ν N-H	ν_{asy} S-O	ν_{sy} S-O	ν S-N	ν S-F
$HN(SO_2F)_2$	3320 br.	1470 vs	1220vs	923s	832s
$ClN(SO_2F)_2$		1495 vs	1231 vs	904	849s
$S_2O_5F_2$		1513 s	1248s		824s
$C_2F_2H_3N(SO_2F)_2$[b]		1471s	1258s	910vs	832s
		1446s	1232s		
$C_4H_9N(SO_2F)_2$[c]		1475s	1248w	922vs	850s
		1465s	1218s		
$C_4H_8ClN(SO_2F)_2$[d]		1475s	1235s	920s	860s
		1445s	1218s		
$C_4H_8ClN(SO_2F)_2$[e]		1480s	1232s	920s	850s
		1450s	1220s		
$C_2F_2H_2ClN(SO_2F)_2$[f]		1490s	1255s	908vs	832s
		1470s	1230s		
$C_2F_2H_2ClN(SO_2F)_2$[g]		1490s	1222s	910s	830s
		1465s			

[a] Infrareds of neat liquids; vs=very strong, s=strong, w=weak

[b] Adduct of $CH_2=CF_2$ and $HN(SO_2F)_2$

[c] Adduct of cis- or trans-2-butene and $HN(SO_2F)_2$.

[d] Adduct of cis 2-butene and $ClN(SO_2F)_2$.

[e] Adduct of trans-2-butene and $ClN(SO_2F)_2$.

[f] Adduct of $CH_2=CF_2$ and $ClN(SO_2F)_2$

[g] Adduct of cis-CHF=CHF and $ClN(SO_2F)_2$.

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TABLE IV

Mass Spectral Data

m/e	I	II	III	IV	V	Assignments
244			4			$C_2H_2F_2N(SO_2F)_2$
230	69	1.5				$CF_2N(SO_2F)_2$
214			9			$CHFN(^{32}SO_2F)(^{34}SO_2F)$
212			100			$CHFN(SO_2F)_2$
210					10*(16)**	$CH_3CHN(^{34}SO_2F)(^{32}SO_2F)$
209					5 (8)	$C_2H_5N(SO_2F)_2$
208				100	100(100)	$CH_3CHN(SO_2F)_2$
188					1.4(3)	$C_2H_3NS_2O_4F$
128	40	5				CF_2NSO_2
124					7(10)	CH_3CNSO_2F
123				3		
110			46		2(1.7)	$CHNSO_2F$
101	21		7			$C_2H_2F_2{}^{37}Cl$
100	8					$C_2HF_2{}^{37}Cl$
99	63		22			$C_2H_2F_2{}^{35}Cl$
98	22		5			$C_2HF_2{}^{35}Cl$
97					1.8(1.7)	NSO_2F
83	44	6	37	2	5(3)	SO_2F
67	17	2	44	2	4(3)	^{34}SOF
65	100	100			4(6)	^{32}SOF
64	15	6			2(1.5)	CH_2CF_2/SO_2

I $CH_2ClCF_2N(SO_2F)_2$

II $CH_3CF_2N(SO_2F)_2$

III $CHFClCHFN(SO_2F)_2$

IV $C_4H_9N(SO_2F)_2$

V $C_4H_8ClN(SO_2F)_2$ *cis-adduct, **trans-adduct