Journal of Fluorine Chemistry, 29 (1985) 311–322

Received: December 5, 1984; accepted: April 7, 1985

REACTION OF TRIHALOGENMETHANESULFENYL CHLORIDES, ACETATES AND TRIFLUOROACETATES WITH NORBORNENE

A. HAAS, M. LIEB and Yuanfa ZHANG

Lehrstuhl für Anorganische Chemie II der Ruhr-Universität Bochum,
Postfach 10 21 48, D-4630 Bochum 1 (F.R.G.)

SUMMARY

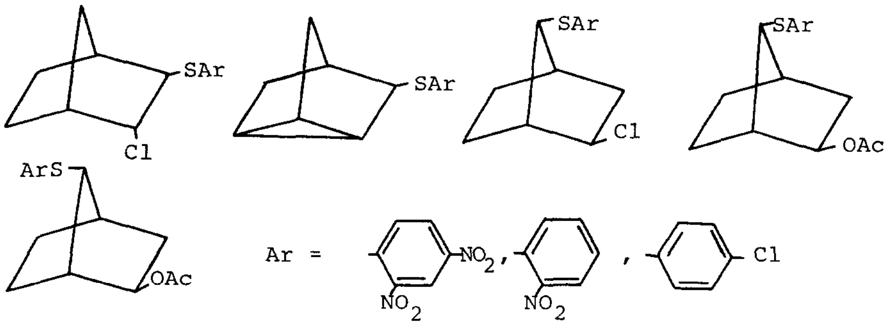
The reaction of trihalogenomethanesulfenyl chlorides, acetates and trifluoroacetates, RSX R = CF_3, CF_2Cl, $CFCl_2$, CCl_3; X = Cl, $CH_3C(O)O$, $CF_3C(O)O$ with norbornene proceeded with skeletal rearrangement. According to the reactants used, 2-endo-X-3-exo-(SR)-norbornanes, 3-(SR)-nortricylanes, 2-exo-X-7-syn- and -anti-(SR)-norbornanes were formed. The factors influencing the reaction course are discussed.

INTRODUCTION

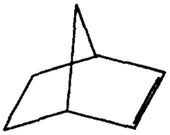
Reactions of norbornene (1) with strong electrophiles are often accompanied by the Wagner-Meerwein rearrangement. Sulfenyl chlorides, which are usually considered weak electrophilic reagents, when reacted with 1 rarely induce skeletal rearrangement [1,2,3]. It was postulated that the formation of rearranged products could be possible with sulfenyl chlorides of greater electrophilicity. Zefirov et al. [4] found a small quantity of rearranged products in the reaction of norbornene with 2,4-dinitrobenzenesulfenyl chloride. They also found a new method for increasing the electrophilicity of sulfenyl chlorides by addition of $LiClO_4$ to the reaction system or by using a highly ionizing solvent, e.g. CH_3COOH. Under these conditions the reaction of 1 with ArSCl gave the following products which were isolated and characterized [4,5].

0022-1139/85/$3.30

RESULTS



In the present work, we studied the reaction of 1 with trihalogenomethanesulfenyl chlorides (2), acetates (3) and trifluoroacetates (4).

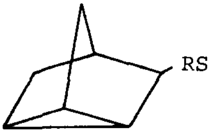


1

+ $CF_nCl_{3-n}SCl$, $AcOSCF_nCl_{3-n}$, $CF_3COOSCF_{n'}Cl_{3-n'}$

2 3, (n = 0-3), 4, (n' = 1,2,3)

It was found that these reactions proceeded with skeletal rearrangements even in the absence of external substances (e.g. $LiClO_4$) or polar solvents. Rearranged products included 2,3-trans adducts and 3-substituted nortricylenes as follows.



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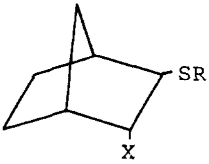
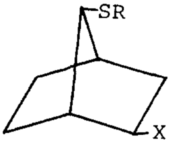
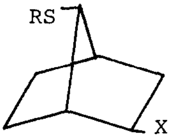






X	
Cl	6
$CH_3C(O)O$	9
$CF_3C(O)O$	12

	X	
7	Cl	8
10	$CH_3C(O)O$	11
13	$CF_3C(O)O$	14

R = CF_3, CF_2Cl, $CFCl_2$, CCl_3
a b c d

Reactions of **1** with **2**

Norbornene, unlike most alkenes, reacted readily with **2** even in the absence of a catalyst or solvent. The reactivity of **2** increased with the number of fluorine atoms. In the case of CF_3SCl, the reaction proceeded vigorously even at temperatures below -40°C, yielding 3-trifluoromethylmercaptonortricylane (**5a**), 2-endo-chloro-3-exo-trifluoromethylmercaptonorbornane (**6a**), 2-exo-chloro-7-syn-(**7a**)-and-anti-trifluoromethylmercaptonorbornane (**8a**). With **1**, both **2b** and **2c** also reacted rapidly at 0 to 20°C, giving mainly the 2,3-trans adducts **6b** and **6c** as well as the 3-substituted nortricylenes **5b** and **5c**, respectively; however, no rearranged products were found. With **1**, **2d** afforded upon heating only **6d**. The reaction results (yield in % determined by ^{1}H-NMR-spectroscopy) are listed below.

2	**5**	**6**	**7**	**8**
a	33	7	15	20
b	56	28	--	--
c	21	61	--	--
d	--	93	--	--

Reactions of **1** with **3**

The reactions of **1** with **3** afforded significant amounts of nortricylenes **5**. In addition, the 2,3-trans adducts **9** and rearranged products **10** and **11** were observed, with **3** (n = 0), only upon heating or in acetic acid at ambient temperature. Distribution of products (yield in %) obtained by isolation and by ^{1}H-NMR analysis are as follows.

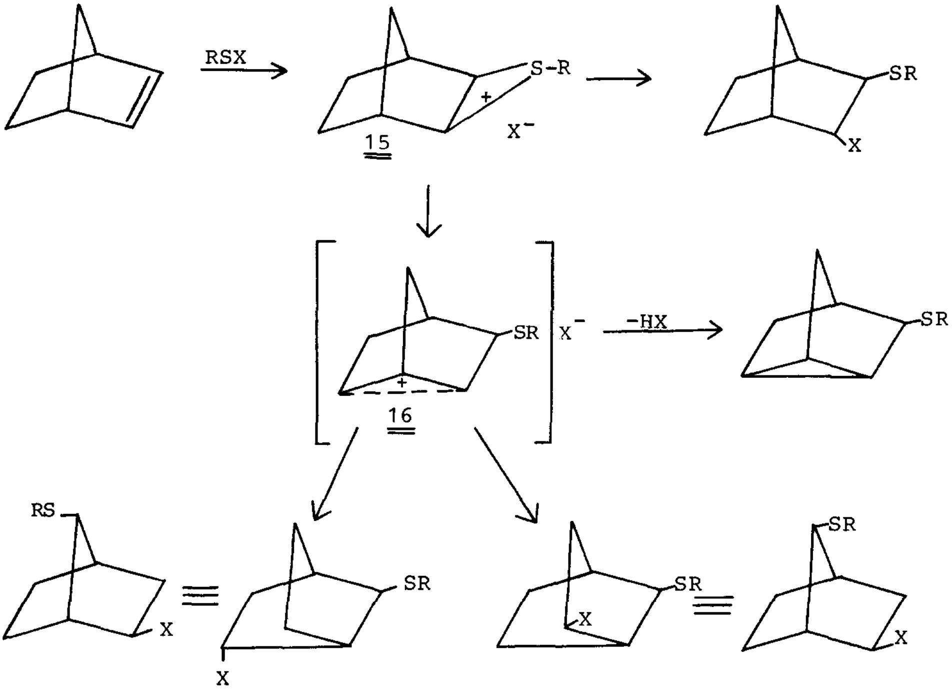
3	**5**	**9**	**10**	**11**
a	64	4	9	12
b	65	6.5	20.5	5
c	54	13	10.5	13.5
d	25	16	33	16

Reactions of **1** with **4**

A vigorous and exothermic reaction took place between **1** and **4** even at temperatures below -40°C. When the reaction was carried out at temperatures of -40 to 0°C in n-pentane, considerable amounts of rearranged products **13** and **14**, 2,3-trans adducts **12** and nortricylenes **5** were formed. Yields in % and products are given below.

4	**5**	**12**	**13**	**14**
a	39	6	15	20
b	9	5	17	25
c	13	11	15	23

The mechanism for the reaction of **1** with sulfenyl chlorides has received considerable attention. A generally postulated nonclassical norbornyl carbonium ion intermediate **16** can be used to explain the formation of rearranged products as shown below. It is apparent that the tendency for rearrangement depends markedly on the nature of R and X. The strong electron withdrawing CF_3-group is assumed to be most favoured for transition from an episulfonium ion **15** to a norbornyl carbonium ion **16**, hence, most liable to form rearranged products.



R = CF_3, CF_2Cl, $CFCl_2$; X = Cl, AcO, CF_3COO

Although reaction with CF_3SCl yielded products **7** and **8**, no rearrangement products were detected with the sulfenyl chlorides **2b** - **d**. This effect of the anionic moiety on the distribution of products is also evident with acetates. The reaction of **1** with **4** afforded mainly rearranged products **13** and **14**.

Spectroscopic characterization

The structural determinations of the products were achieved by ^1H-, ^{13}C-NMR, IR, MS and elemental analyses. ^1H-NMR data are provided in Table 1. The structures of nortricyclenes **5** were confirmed by comparison of their spectral data with those of ana-

TABLE 1

Reaction of Norbornene with Fluorochloromethanesulfenyl Chlorides, Acetates and Trifluoroacetates

Reactants				Reaction Conditions			
Norbornene (g (mmol)	$CF_nCl_{3-n}SX$ g(mmol)	n	X	Temp. (°C)	Time (hrs.)	Solvent (ml)	Yield (%)
9 (96)	13.2 (97)	3	Cl	-40 to 20	1	--	85
5 (53)	7.7 (50)	2	Cl	0 to 20	1	--	84
5 (53)	8.6 (51)	1	Cl	20	2	--	81
5 (53)	9.3 (50)	0	Cl	80 to 90	2	--	93
6.5 (69)	10.0 (63)	3	AcO	0	4	--	85
3.5 (37)	5.2 (30)	2	AcO	20	4	--	97
7.4 (79)	12.7 (66)	1	AcO	20	12	--	94
5 (53)	9.0 (43)	0	AcO	80 to 90	3	--	79
5 (53)	10.0 (48)	0	AcO	20	72	CH_3COOH (10)	82
5 (53)	7.0 (33)	3	CF_3COO	-40 to 10	1	n-Pentane (30)	80
8 (85)	15.8 (69)	2	CF_3COO	-40 to 10	1	n-Pentane (30)	57
9.4 (100)	16.5 (67)	1	CF_3COO	-40 to 10	1	n-Pentane (50)	62

logous 3-substituted nortricylanes. The IR spectra of 5 have the characteristic absorption of nortricylene at about 820 cm^{-1}[1,6]. Their mass spectral data are compatible with those of 3-chlor-nortricylene [7]. ^{13}C-NMR spectral data (Table 2) are closely consistent with 3-nortricylanol [8]. The structural assignments of 2,3-trans adducts 6, 9 and 12 are based mainly on the characteristic NMR-signals of the methine hydrogens. Each spectrum of 6 (X = Cl) has a doublet of triplets at about 4.1 ppm (J ≈ 4.0 and 1 Hz) for 2-H and a doublet of doublets at about 3.2 ppm (J = 4.5 and 2.0 Hz) for 3-H. These parameters are consistent with those of 2-endo-chloro-3-exo-phenylmercapto norbornene [3]. The structure of the other 2,3-trans adducts (9 and 12) were also confirmed by comparison of their NMR spectral data with those of authentic 2,3-trans norbornanes [9, 10, 11]. The rearranged products 7, 10, 13 and 8, 11, 14 were identified by comparison of their spectra with those of 2-exo-acetoxy-7-syn-and-anti-(2.4-dinitrophenylmercapto)norbornane [4], whose molecular structure had been determined by an X-ray diffraction analysis [12]. The singlet or sharp multiplet for H-C-S suggested the RS-group occupied the 7-position in both isomers 7, 10, 13 and 8, 11, 14. The 2-exo-position of X was assigned, based on a broad signal ($\tau_{1/2}$ = 11 - 13 Hz), for H-C-Cl at about 4.00 ppm, H-C-OAc at about 4.7 ppm and H-C-$OCOCF_3$ at about 4.9 ppm. The distinction between syn and anti isomeric pairs is based on the position of δ(7-H). This signal appeared at lower field for the syn-isomer than for the anti-isomer. In addition, for 2,3-trans adducts (6, 9, 12) δ(3-H) appeared at lower field than for all other adducts. That enabled the determination of the isomeric ratio in each mixture by comparison of the relative intensity of the signals.

TABLE 2

Physical and Analytical Data of Products of Norbornene-Perhalogenomethanesulfenyl Chloride, Acetate and Trifluoroacetate Reactions

Compound	Formula (Mol. weight)	Bp. °C (mm)	C %		H %	
			Calc.	Found	Calc.	Found
5a	$C_8H_9F_3S$ (194.2)	45 - 47 (10)	49.41	48.9	4.67	4.6
5b	$C_8H_9ClF_2S$ (210.7)	75 - 78 (10)	45.60	45.1	4.30	4.3
5c	$C_8H_9Cl_2FS$ (227.1)	50 - 52 (0.1)	42.31	40.9	3.99	3.8
6a, **7a**, **8a**	$C_8H_{10}ClF_3S$ (230.7)	86 - 90 (10)	41.65	41.5	4.37	4.6
6b	$C_8H_{10}Cl_2F_2S$ (247.1)	47 - 48 (0.07)	38.89	38.8	4.08	4.2
6c	$C_8H_{10}Cl_3FS$ (263.6)	62 (0.08)	36.45	36.5	3.82	4.0
6d	$C_8H_{10}Cl_4S$ (280.0)	83 - 85 (0.05)	34.31	34.3	3.60	3.8
9a, 10a, 11a	$C_{10}H_{13}F_3O_2S$ (254.3)	50 - 55 (0.08)	47.19	46.8	5.15	5.4
9b, 10b, 11b	$C_{10}H_{13}ClF_2O_2S$ (270.7)	68 - 70 (0.05)	44.37	44.1	4.84	5.1
9c, 10c, 11c	$C_{10}H_{13}Cl_2FO_2S$ (287.1)	80 - 83 (0.1)	41.83	41.7	4.56	4.8
9d, 10d, 11d	$C_{10}H_{13}Cl_3O_2S$ (303.5)	86 - 89 (0.08)	39.57	39.8	4.32	4.6
12a, 13a, 14a	$C_{10}H_{10}F_6O_2S$ (308.3)	70 - 75 (10)	38.96	38.8	3.27	3.5
12b, 13b, 14b	$C_{10}H_{10}ClF_5O_2S$ (324.7)	55 - 58 (0.07)	36.99	36.6	3.10	3.2
12c, 13c, 14c	$C_{10}H_{10}Cl_2F_4O_2S$ (341.1)	68 - 75 (0.08)	35.21	35.2	2.96	3.2

EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer 325 infrared spectrophotometer. Liquids were measured as capillary films between KBr plates. Weak bands and shoulders are not reported.

^{1}H-NMR spectra were obtained on a Bruker WP 80 SY, ^{19}F- and ^{13}C-NMR spectra were recorded on a Bruker WM 250 PFT-spectrometer. ^{1}H- and ^{13}C-NMR were recorded in $CDCl_3$ solution, using $Si(CH_3)_4$ as an internal standard. ^{19}F-NMR-spectra were measured in C_6F_6 solution.*

Mass spectra were recorded on a Varian MAT spectrometer CH 7 at an energy of 70 eV and 100µA.

Starting materials: Sulfenylacetates [13] and sulfenyltrifluoroacetates [14] were prepared via literature methods.

Gas chromatography: Perkin-Elmer F 21 Gas chromatograph. Preparative columns of 20 % OV 275 Chromosorb P AW 45-60 mesh or 10 % OV 101 Chromosorb P AW 45-60 mesh.

Reactions of norbornene with $CF_nCl_{3-n}SX$ (X = Cl, $CH_3C(O)O$, $CF_3C(O)O$ and n = 0, 1, 2, 3)

Into the norbornene contained in a 250 ml three necked flask equipped with a dropping funnel, stirrer, and condenser, was dropped $CF_nCl_{3-n}SX$. As the mixture was stirred at ambient temperature, an exothermic reaction occured. The reaction mixture was distilled *in vacuo*. Further purification of the initial fractions was achieved by redistillation or gas chromatography.

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*All values calibrated against CF_3Cl.

Amounts of reactants, reaction conditions, yields, and solvents are given in Table 1; boiling points and elemental analysis in Table 2. ^{1}H-, ^{19}F- and ^{13}C-NMR data are provided in Tables 3 and 4.

Mass-spectra: **5a** 194, M^+ (18), 125 (9), 93 (100), 91 (51), 79 (13), 77 (39), 69 (6), 66 (20), 65 (14).

5b 212 (4), 210, M^+ (9), 125 (6), 93 (100), 91 (42), 85 (4), 79 (7), 77 (30), 66 (19), 65 (11).

5c 228 (3, 5), 226, M^+ (5), 125 (6), 93 (100), 91 (39), 79 (6), 77 (29), 66 (8), 65 (10).

IR: **5a** 3070 (m), 2955 (vs), 2880 (s), 1450 (m), 1305 (s), 1256 (s), 1225 - 1235 (m, br), 1060 - 1190 (vs), 960 (m), 910 (m), 815 (s), 760 (s) cm^{-1}.

5b 3060 (m), 2940 (vs), 2875 (s), 1445 (m), 1295 (s), 1250 (m), 1000 - 1140 (vs, br), 825 - 935 (vs), 807 (s), 765 (s) cm^{-1}.

5c 3070 (m), 2940 (vs), 2876 (s), 1448 (m), 1300 (s), 1250 (m), 970 - 1085 (vs), 780 - 880 (vs), 765 (vs), 530 (m) cm^{-1}.

9a, **10a**, **11a** 2950 (vs), 2880 (s) cm^{-1}, norbornyl; 1730 cm^{-1} (vs), C=O; 1190 - 1290 cm^{-1} (vs), CF_3.

12a, **13a**, **14a** 2970 (vs), 2890 (s) cm^{-1}, norbornyl; 1785 (vs) cm^{-1} , C=O; 1100 - 1250 (vs), CF_3.

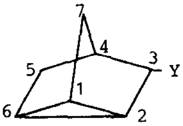
TABLE 3

^{1}H- and ^{19}F-NMR-Spectral Data of Selected Fluorochloromethylmercapto Derivatives

Cmpd.	^{1}H Chemical Shifts	^{19}F	
5a	1.25 (s, 3H), 1.36 - 1.44 (m, 3H), 1.64 - 1.84 (m, 1H) 2.13 (s, 1H), 3.20 (s, 1H)	40.5	
5b	1.28 (s, 3H), 1.33 - 1.48 (m, 3H), 1.60 - 1.80 (m, 1H) 2.16 (s, 1H), 3.28 (s, 1H)	25.7	
5c	1.30 (s, 3H), 1.33 - 1.50 (m, 3H), 1.62 - 1.80 (m, 1H) 2.24 (s, 1H), 3.36 (s, 1H)	16.4	
7a	1.2 - 2.4 (m, 6H), 2.4 - 2.6 (m, 2H), 3.3 (s, 1H), 3.92 (dt, J 4.6 and 1.2 Hz, 1H)	41.2	
8a	1.05 - 2.2 (m, 6H), 2.3 - 2.6 (m, 2H), 3.78 (s, 1H), 3.95 (dd, J 4.3 and 2.9 Hz, 1H)	43.2	
6b	1.25 - 2.2 (m, 6H), 2.3 - 2.6 (m, 2H), 2.15 (dd, J 2.4 and 1.9 Hz, 1H), 4.05 (dt, J 4.0 and 1 Hz, 1H)	26.4	
6c	1.25 - 2.2 (m, 6H), 2.3 - 2.6 (m, 2H), 3.22 (m, 1H), 4.22 (dt, J 4.2 and 1 Hz, 1H)	18.4	
6d	1.25 - 2.2 (m, 6H), 2.4 - 2.7 (m, 2H), 3.25 (dd, J 4.5 and 2 Hz, 1H), 4.14 (dt, J 4.4 and 1 Hz)	--	
9a	1.2 - 1.9 (m, 6H), 2.07 (s, 3H), 2.38 (m, 1H), 2.64 (m, 1H), 3.02 (t, J 3.6 Hz, 1H), 4.85 (t, J 4.0 Hz, 1H)	40.2	
10a	1.2 - 1.9 (m, 6H), 2.0 (s, 3H), 2.48 (m, 2H), 3.24 (sharp m, 1H) 4.66 (dt, 1H)	42.0	
11a	1.2 - 1.9 (m, 6H), 2.02 (s, 3H), 2.42 (m, 2H), 3.53 (s, 1H), 4.69 (dd, J 7.2 and 2.6 Hz, 1H)	41.1	
13a	1.2 - 2.2 (m, 6H), 2.6 (m, 2H), 3.30 (s, 1H), 4.87 (t, J 6.0 Hz, 1H),	42.0	7
14a	1.2 - 2.2 (m, 6H) 2.4 - 2.65 (m, 2H), 3.55 (s, 1H), 4.92 (dd, J 4.8 and 2.8 Hz, 1H)	41.1	7

TABLE 4

Carbon-13 Chemical Shifts of 3-substituted Nortricylenes

Compound	Y	^{13}C Chemical Shifts						
		C-1	C-2	C-3	C-4	C-5	C-6	C-
	SCF_3	12.2	15.0	49.4	35.5	30.0	10.6	32
	SCF_2Cl	12.1	14.8	51.1	35.3	30.1	10.6	32
	$SCFCl_2$	12.0	14.6	53.8	35.1	30.3	10.7	32
	OH [8]	13.2	15.9	77.0	35.6	29.4	10.7	30

ACKNOWLEDGEMENTS

The authors thank Prof. Dr. K. E. Peterman for helping with the English manuscript. One of us (Y. Z.) gratefully acknowledges the Heinrich-Hertz-Stiftung for a two-year grant.

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