Journal of Fluorine Chemistry, 12 (1978) 257–270

Received: February 16, 1978

REGIO- AND STEREOSPECIFIC HALOGENATION OF HALOGENOALKENES IN LIQUID HYDROGEN FLUORIDE

L. S. Boguslavskaya, N. B. Melnikova, A. P. Voronin and V. R. Kartashov.

Kargin Polymer Research Institute, Dzerzhinsk, Gorky region, 606006 USSR

SUMMARY

The products of bromo and chlorofluorination of E and Z-1, 2-dichloroethylenes, 1, 3-dichloro-1-propenes, 1, 1-dichloroethylene and 1,3-dichloro-2-fluoro-1-propene by N-bromosuccinimide and hexachloromelamine in anhydrous hydrogen fluoride have been studied. It was found that the reaction was in all cases 100% regio and 93-100% trans-stereospecific with the exception of E-1, 2-dichloroethylene, its trans-stereospecificity being 85%.

Threo and erithro-1-bromo-1, 2-dichloro-2-fluoroethanes, 2-bromo-1, 3-dichloro-1-fluoropropanes and 1, 2, 3-trichloro-1-fluoropropanes as well 1, 1, 2-trichloro-2-fluoroethane, 1-bromo-2, 2-dichloro-2-fluoroethane, 1, 2, 2-trichloro-2-fluoroethane, 1-bromo-1, 3-dichloro-2, 2-difluoropropane, and 1, 1, 3-trichloro-2, 2-difluoropropane were obtained in 50-70% yield.

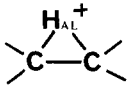
The bromination of E and Z-1, 3-dichloro-1-propenes with molecular bromine in carbon tetrachloride in the dark is non-stereospecific and gives a mixture of erithro and threo-1, 2-dibromo-1, 3-dichloropropanes in the ratio about 1:1. However, the bromination reaction in anhydrous hydrogen fluoride solution proceeds with a high degree of stereospecificity (94-95%) and gives threo-1, 2-dibromo-1, 3-dichloropropane from Z and erithro-1, 2-dibromo-1, 3-dichloropropane from E-1, 3-dichloro-1-propene.

The data obtained are considered in terms of an electrophilic mechanism of halogenoalkene halogenation in anhydrous hydrogen fluoride and a free-radical mechanism in carbon tetrachloride.

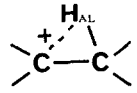
INTRODUCTION

Alkenes, having halogens in the 1-position of a terminal double bond, react with molecular halogens by a free-radical mechanism [1-3].

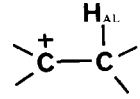
However, it has been pointed out that, by the action of N-halogenoamides on some of the above halogenoalkenes in anhydrous hydrogen fluoride as a solvent, "Hal F" polar addition to the double bond proceeds smoothly [4, 5]. The polar halogenation of most alkenes is trans-stereospecific. This can be explained by the formation of bridged halogen intermediates of symmetrical (A) and unsymmetrical (B) types followed by a nucleophilic attack from the side opposite to the bridge [6-8].



A



B



C

The formation of the carbenium ion intermediate of the open type (C) [8] and non-stereospecific halogenation of the double bond [9-13] are favoured by substituents at the double bond, capable of delocalisation of the positive charge of the carbenium ion (Ar, Ro).

Halogen substituents at the 2-position of the terminal double bond also favour carbenium ion stabilisation (C)[14] and greatly increase regiospecificity of the halogenation reaction and the halogenofluorination of the allylic systems in particular [15-17].

In this work "BrF", "ClF" and Br_2 addition to the double bond of some symmetrical and unsymmetrical dihalogenoalkenes, were studied in an attempt to determine the effect of 1-vinylhalogen substituents on the orientation and stereochemistry of the polar halogenation in liquid hydrogen fluoride and to determine, in this way, the possible regio- and stereospecific syntheses of halogenofluoroalkanes.

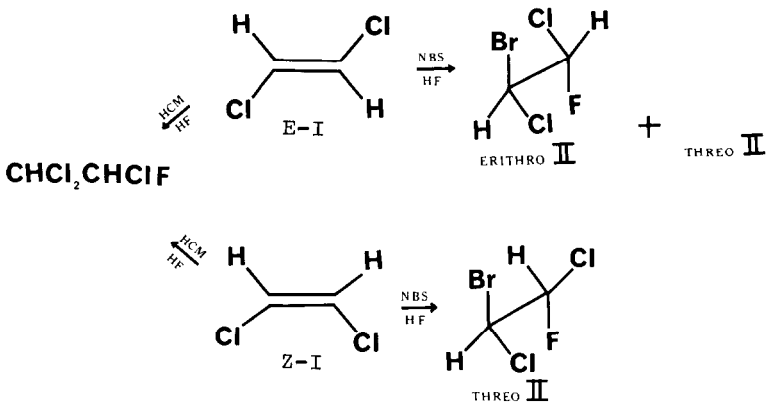
DISCUSSION

E- and Z-, 2-dichloroethylenes, E- and Z-1, 3-dichloro-1-propenes, 1, 1-dichloroethylene and E-1, 3-dichloro-2-fluoro-1-propene were used as model compounds; N-bromosuccinimide (NBS), hexachloromelamine (HCM) and molecular bromine (Br_2) were used as sources of electrophilic halogens; anhydrous hydrogen fluoride was used as a fluorine anion donor, being at the same time a solvent in the halogenation reactions.

The extent of isomerisation of chosen model compounds was initially investigated. The compounds were kept in liquid hydrogen fluoride solution at the reaction conditions (3-3$\frac{1}{2}$ hours at -20 to + 10°C). Only E-1, 3-dichloro-1-propene was isomerised under these conditions. After 3$\frac{1}{2}$ hours a mixture of 88-90% E and 10-12% Z-isomer was obtained.

In all cases the halogenofluorination reaction proceeds smoothly yielding 50-70% of "Hal F" addition products to the double bond. Regio- and stereospecificity of the reaction was assigned of the basis of ^{1}H NMR spectra of the reaction products and by the double resonance method (INDOR) to determine the interacting lines in the AB and A_2B multiplets for halogenoethanes and halogenopropanes respectively.

SCHEME 1

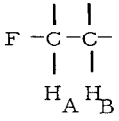


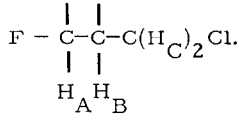
"BrF" addition to Z-1,2-dichloroethylene (Z-I) proceeds in a trans-stereospecific fashion with the formation of threo-1-bromo-1,2-dichloro-2-fluoroethane (threo-II). "BrF" addition to E-1,2-dichloroethylene (E-I) proceeds predominantly trans-stereospecifically with the formation of 85 ± 3% erithro-II and 15 ± 3% threo-II mixtures.

TABLE 1

Data of the ^{1}H NMR spectra of halogenoalkanes[a]

Compound	δ			J, Hz.				
	H_A	H_B	H_C	H_A-F	H_A-H_B	H_B-F	H_B-H_C	
erithro-CHClFCHClBr	6.20	5.83	-	53.6	3.4	16.2	-	II
threo-CHClFCHClBr	6.17	5.81	-	51.2	3.8	12.5	-	II
$CHClFCHCl_2$	6.16	5.79	-	52.6	3.7	13.0	-	III
CH_2Br-CCl_2F	-	4.05	-	-	-	13.8	-	V
CCl_3CH_2Br	-	4.21	-	-	-	-	-	VI
CCl_2FCH_2Cl	-	4.07	-	-	-	13.4	-	VIII
threo-$CHClFCHBrCH_2Cl$	6.37	4.36	3.90	49.5	4.0	14.8	6.0	X
erithro-$CHClFCHBrCH_2Cl$	6.41	4.45	3.89	48.7	3.0	9.2	6.7	X
$CHCl_2CHBrCH_2Cl$	6.16	4.53	3.97	-	3.2	-	6.5	XI
threo-$CHClF$-$CHClCH_2Cl$	6.34	4.24	3.85	49.3	4.3	13.4	6.0	XII
erithro-$CHClFCHClCH_2Cl$	6.45	4.30	3.77	48.7	3.4	9.4	5.7	XII
threo-$CHClBrCHBrCH_2Cl$	6.13	4.45	3.92	-	2.7	-	6.6	XIII
erithro-$CHClBrCHBrCH_2Cl$	6.10	4.55	3.90	-	3.2	-	7.0	XIII
$CHClBrCF_2CH_2Cl$	6.03	-	3.96	10.0	-	-	-	XV
$CHCl_2CF_2CH_2Cl$	5.94	-	3.94	8.3	-	-	-	XVI

Note: a) halogenoethanes:  ;

halogenopropanes:  .

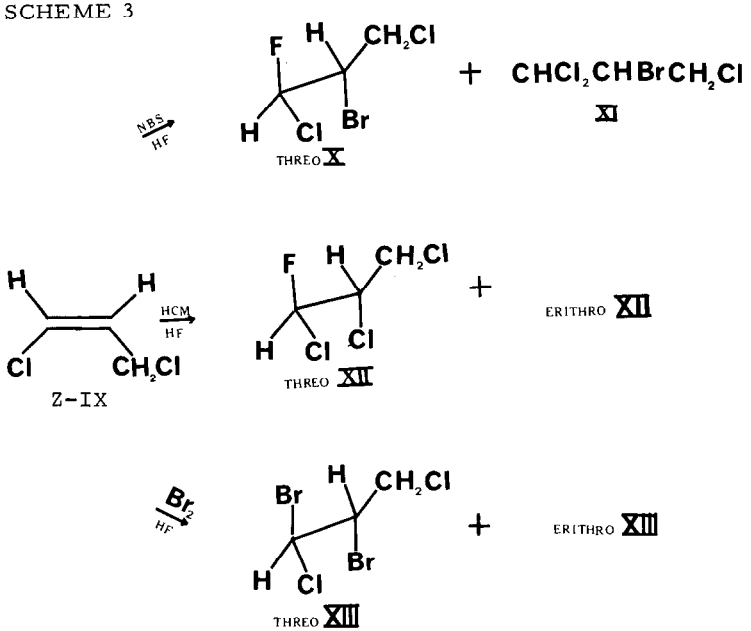
Chemical shifts and coupling constants of threo- and eritho-II substantially differ (table 1) and to reliably identify these stereoisomers ^{1}H NMR spectra may be used. Chlorofluorination of Z-1 and E-1 gives 1,1,2-trichloro-2-fluoroethane (III). Halogenofluorination of 1,2-dichloroethylenes showed no noticeable side products. When a mixture of solvents HF, CH_3OH and $CHCl_3$ (molar ratio 2:1:2) was used instead of pure hydrogen fluoride the stereospecificity of the bromofluorination reaction of olefines-I was unchanged.

Bromo- and chlorofluorination of 1,1-dichloroethylene (IV) (Scheme 2) proceeds regiospecifically and gives, accordingly, 1-Br-2,2-dichloro-2-fluoroethane (V) and 1,2,2-trichloro-2-fluoroethane (VIII). Bromofluorination (IV) gave an unexpected side product 1-bromo-2,2,2-trichloroethane (VI) and a small quantity of 1-bromo-2,2-dichloroethylene (VII).

SCHEME 2

$$\underset{\text{VIII}}{CH_2ClCCl_2F} \xleftarrow[(HF)]{HCM} \underset{\text{IV}}{CH_2{=}CCl_2} \xrightarrow[(HF)]{NBS} \underset{\text{V}}{CH_2BrCCl_2F} + \underset{\text{VI}}{CH_2BrCCl_3} + \underset{\text{VII}}{CHBr{=}CCl_2}$$

SCHEME 3



Halogenofluorination of Z and E-1, 3-dichloro-1-propenes proceeds in an entirely regio-specific way, so that the electrophilic halogen (Br, Cl) is directed to the central carbon atom and the fluorine-anion to the CHCl group (Schemes 3, 4).

Thus, bromofluorination of Z-IX yields a single product: threo-2-bromo-1, 3-dichloro-1-fluoropropane (threo-X); a non-fluorinated halogenoalkane 2-bromo-1, 1, 3-trichloropropane (XI) (scheme 3) is a side product of this reaction, which is easily separated from the main product. Chlorofluorination of Z-IX also gives threo-1, 2, 3-trichloro-1-fluoropropane (threo XII) in a high yield (65%), however, its diastereomer (erithro-XII) forms in 5% yield, trans-stereospecificity of the addition being 93% (table 2).

Bromo- and chloro-fluorination of olefine E-IX (scheme 4) proceeds 100% regio- and trans-specifically and yields accordingly, halogenofluoroalkanes erithro-X and erithro-XII (table 2), however, due to E-IX rearrangement the reaction products contain threo-X and threo-XII diastereomers contaminations.

SCHEME 4

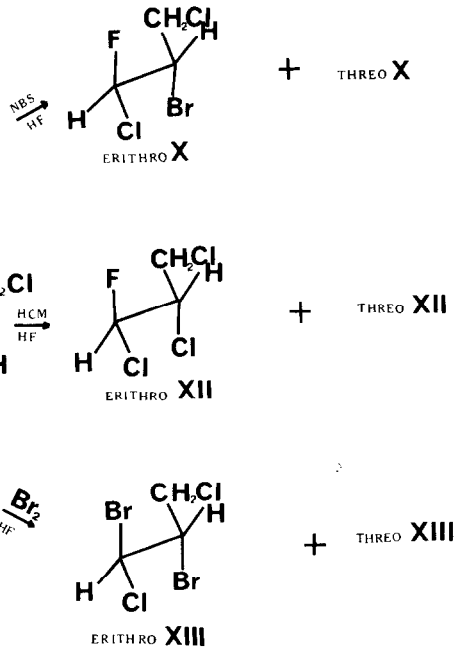
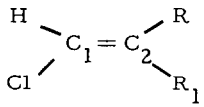


TABLE 2

Regio- and stereospecificity of halogenoalkenes



halogenation in anhydrous hydrogen fluoride at -20 to + 10°C

R	R^1	Agent (Solvent)	Regiospecificity		Halogenation stereospecificity % trans
			C_1F-C_2Hlg	C_1Hlg-C_2F	
H	Cl	NBS[a](HF)	-	-	100[c]
Cl	H	NBS(HF)	-	-	85[c]
H	CH_2Cl	NBS(HF)	100	0	100[c]
CH_2Cl	H	NBS(HF)	100	0	100(93)[d]
H	CH_2Cl	HCM[b](HF)	100	0	93[c]
CH_2Cl	H	HCM(HF)	100	0	100(87.5)[d]
H	CH_2Cl	$Br_2(CCl_4)$	-	-	50
CH_2Cl	H	$Br_2(CCl_4)$	-	-	50
H	CH_2Cl	Br_2(HF)	-	-	94[c]
CH_2Cl	H	Br_2(HF)	-	-	100(94)[d]
CH_2Cl	F	NBS(HF)	0	100[c]	-
CH_2Cl	F	HCM(HF)	0	100[c]	-

a) N-bromosuccinimide
b) Hexachloromelamine
c) The initial halogenoalkene does not isomerize in HF solution in the reaction conditions
d) The initial halogenoalkene isomerizes in HF solution in the experimental conditions and yields a mixture of 88% E- and 12% Z-1,3-dichloro-1-propene.

In the brackets trans-adduct content in the reaction product is given

The stereospecificity of the reaction was determined with regard to the fact that E-IX undergoes rearrangement to Z-IX (10-12%) in liquid hydrogen fluoride. As the relative rates of the rearrangement and those of the halogenofluorination reaction were not determined, the trans-stereospecificity was taken as 100%, if the cis-adduct fraction in the trans-adduct was less than the rearranged Z-IX fraction in E-IX. In other cases when the initial olefines were not rearranged in the reaction conditions, the trans-stereospecificity of the halogenation reaction was considered equal to the percentage of the trans-adduct in the reaction product (table 2). The configurations were attributed to the threo- and erithro-compounds (trans-addition) by analogy with the halogenation reactions of unsubstituted olefines, which proceeds, as is generally known by trans-addition [18].

It is interesting to note the difference in the addition reaction stereospecificity of the molecular bromine to E-X and Z-X alkene double bonds in the non-polar solvent CCl_4 in the dark and in liquid hydrogen fluoride. Though in carbon tetrachloride solution the addition reaction proceeds non-stereospecifically and yields two diastereomeric 1,2-dibromo-1,3-dichloropropanes (threo- and erithro-XIII) in the ratio about 1:1 the molecular bromine addition by a double bond in HF solution proceeds highly stereospecifically (94%).

In this case only bromination, but not bromofluorination takes place. Configurations threo-XIII from Z-IX and erithro-XIII from E-IX were attributed by analogy with the above examples (scheme 3 and 4).

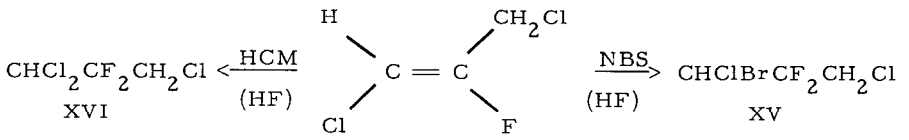
Identification and quantitative determination of the diastereomers (XIII) using ^1H NMR-spectra is not difficult (table 1) and may be done on H_B proton multiplets attached to the central carbon atom.

For the above mentioned halogenofluoropropane diastereomer pairs the difference in ^1H NMR spectra is still more pronounced. In all cases the determination of the diastereomers in the mixture may be done with no more than $\pm$ 2% error.

It was interesting to determine the effect of fluorine atom substitution for the 2-vinyl hydrogen atom in alkene-IX on the regio-specificity of

the halogenofluorination reaction. To this end we have synthesized Z-1, 3-dichloro-2-fluoro-1-propene (Z-XIV).

SCHEME 5



Z-XIV

It appeared that in this case the direction of addition of the reaction is completely changed and it proceeds in such a way, that the electrophilic halogen is directed to the terminal carbon atom of the CHCl-group and the fluorine-anion is directed to the central C-F carbon (scheme 5). 1-Bromo-1, 3-dichloro-2, 2-difluoropane (XV) and 1, 1, 3-trichloro-2, 2-difluoropropane (XVI) were obtained as the only reaction products, which were identified using ^{1}H NMR-spectra (table 1).

The consideration of the given experimental material leads to the conclusion that the halogenation of alkenes with halogen substituents at the 1-vinyl position of the double bonds, in liquid hydrogen fluoride, proceeds by an electrophilic mechanism, and that in non-polar solvents, such as CCl_4, proceeds by a free-radical mechanism. Chlorine as a substituent at the double bond in 1, 3-dichloro-1-propene provides a complete control of the regio-specificity of the electrophilic reaction. On the basis of the data on the stereospecific addition it may be stated that the presence of a single 1-vinyl chlorine atom is not enough for the carbonium ion intermediate in the first stage of the process to be of the open type (C).

It is the most probable that in this case the intermediate has an unsymmetrical partly bridged structure of the B-type with hindered rotation about the C-C bond. It should be noted that the data obtained on the regiospecificity of the electrophilic halogenofluorination of 1, 3-dichloro-1-propene contradicts with the data on the regiospecificity of hypohalogenation of the alkene [19]. The analysis of the experimental

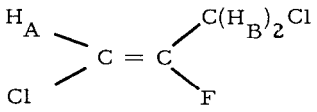
data of this work [19] suggests that the authors obtained a side product of the reaction instead of the main one (15% yield).

It is interesting to note the competitive effect of the vinyl substituents Cl and F in the alkene-XIV on the halogenofluorination regiospecificity.

However, these results cannot be assigned only to the predomination of the "back-donation" effect of fluorine in comparison with chlorine, becau the CH_2Cl-group can also contribute to the carbenium ion intermediate stabilization. We shall further continue our studies in this direction.

EXPERIMENTAL

^1H NMR spectra were recorded using a "Tesla" B487C instrument, working frequency 80 MHz, with hexamethyldisiloxane as internal standard, run at 70°C. Chromatographically pure preparations of E and Z-1, 2-dichloroethylenes (E-I and Z-I) [20] and 1, 1-dichloroethylene (IV) [21] were used. An E and Z-1, 3-dichloro-1-propene mixture (E-IX and Z-IX) was synthesised by the method of Hill and Tisher [22]. Pure preparations of E (Bpt. 111. 3°C) and Z (Bpt. 103. 5°C) isomers were separated by efficient rectification, the configurations were assigned on the basis of NMR spectral data and agreed well with those from the literature [23]. Z-1, 3-dichloro-2-fluoro-1-propene (Z-XIV) was obtained by dehydrochlorination of 1, 2, 3-trichloro-2-fluoropropane (XVII). Z-configuration corresponds to the high boiling isomers [17, 24] and is confirmed by its ^1H NMR spectra



[doublet (δH_A 5. 77), $J(H_A\text{-}F)$=22. 8Hz (trans arrangement of H_A and F); doublet (δ_{H_B} 4. 05), $J(H_B\text{-}F)$=18. 6Hz]

SYNTHESIS OF Z-1, 3-DICHLORO-2-FLUORO-1-PROPENE (Z-XIV)

(a) Preparation of 1, 3-dichloro-2-fluoro-propane (XVIII). 238.0g (2M) thionyl chloride was added to a mixture of 113.5g(1M) 2-fluoro-3-chloro-1-propanol [25] and 2 ml dimethylformamide with shaking and cooling at 0°C. The reaction was then heated at 100°C for 4 hours. The excess thionyl chloride was distilled off, then the residue was poured on to ice water. The lower organic layer was dried and distilled. A fraction b. p. 127-128°C, 109g (83% yield), n_D^{20}=1.4340 was obtained.

(b) Preparation of 2-fluoro-3-chloro-1-propene (XIX). 2-Fluoro-3-chloro-1-propene was obtained from 1, 3-dichloro-2-fluoro-propane by dehydrochlorination with molten potassium hydroxide according to the procedure of Bulovyatova, Sineokov and Etlis [26].

(c) Preparation of 1, 2, 3-trichloro-2-fluoropropane (XVII). Carefully dried gaseous chlorine was added to a solution of 47g (0.5M) 2-fluoro-3-chloro-1-propene (XIX) and 300 ml methylene chloride in the dark at such a rate that the temperature of the reaction mixture did not exceed 40°C. The addition was continued until the reaction was complete as evidenced by temperature of the reaction mixture falling to room temperature. The solvent was then distilled off and final distillation gave 58g 1, 2, 3-trichloro-2-fluoropropane (70% yield), b. p. 129-130°C, n_D^{20} 1.4474.

(d) Preparation of Z-1, 3-dichloro-2-fluoro-1-propene (Z-XIV). 1, 2, 3-trichloro-2-fluoro-propane (XVII) 82.7g (0.5M) was added dropwise to 0.6M potassium t-butoxide in t-butanol (23.4g potassium metal in 480 ml t-butanol) with shaking and cooling at 0°C.

The reaction mixture was gradually heated to room temperature and kept there for one hour. The salts of the residue were dissolved in the minimum quantity of ice water. The organic layer was separated and washed several times with water until removal of t-butanol was complete. After drying over $MgSO_4$ and distillation 24.6g (38% yield) Z-1, 3-dichloro-2-fluoro-1-propene (Z-XIV), b. p. 118-118.5°C, d_{20}^4=1.3940, n_D^{20} 1.4550 was obtained [17, 24].

HALOGENOFLUORINATION

0.5M halogenoalkene was added to 89g N-bromosuccinimide (NBS) or 28g (0.5M of active chlorine) hexachloromelamine (HCM) in 50 ml anhydrous hydrogen fluoride at -10^{o} to $0^{o}C$ with shaking. The reaction mixture was heated to room temperature and agitated for several hours till it gave a negative reaction with KI. Then the reaction mixture was added to 200 ml of water, the organic layer was separated, neutralized with aqueous solution of sodium carbonate, dried and distilled at the atmospheric pressure or under vacuum, depending on the properties of the obtained product. The yield (calculated on alkene) and the properties of the products are given in Table 3.

BROMINATION OF E- and Z-1, 3-DICHLOROPROPENES

(a) The alkene (equimolecular quantity) was added to 100 ml 0.4M solution of bromine in carbon tetrachloride at room temperature in the dark; the reaction mixture was agitated till it gave a negative reaction with KI. After distilling off the solvent and distillation of the reaction product under vacuum, 1,2-dibromo-1,3-dichloro-propane was obtained in a high yield 16.8g (95%).

(b) The bromination was conducted in liquid hydrogen fluorine by analogy with halogenofluorination reactions, using molecular bromine instead of N-halogenoamide. The data are given in table 3.

TABLE 3

Dichloroalkenes halogenofluorination products

	Compound	Yield	B. p.	d_4^{20}	n_D^{20}	MR_D		Found%		
						found	calcu-lated	C	H	F
VIII	CH_2ClCCl_2F	33	88°(760)	1.4915	1.4270	26.08	25.93	15.93	1.35	12.10
II	threo-CHClFCHClBr	48	123°(766)	1.9290	1.4770	28.71	28.83	12.12	1.05	9.55
II	85% erithro- and 15% threo-CHClFCHClBr	50	126°(766)	1.9310	1.4790	28.77	28.83	11.95	1.03	9.48
V	CH_2BrCCl_2F	50	110°(760)	1.8785	1.4660	28.66	28.83	12.40	1.04	9.50
VI	CCl_3CH_2Br	9	152°(760)	1.9140	1.5135	33.40	33.80	11.68	0.88	-
III	$CHClFCHCl_2$	35	101°(752)	1.5378	1.4390	25.80	25.93	15.71	1.38	12.80
XII	93% threo- and 7% eritho-$CHClFCHClCH_2Cl$	70	143°(760)	1.4818	1.4554	30.61	30.02	20.94	2.50	11.47
XII	93% erithro- and 7% threo-$CHClFCHClCH_2Cl$	65	139°(760)	1.4827	1.4550	30.58	30.02	21.03	2.53	11.46
X	threo-$CHClFCHBrCH_2Cl$	52	40° (5)	1.8233	1.4908	33.22	33.45	17.48	1.98	9.00
X	93% erthro- and 7% threo-$CHClFCHBrCH_2Cl$	65	30° (4)	1.8258	1.4900	33.33	33.45	17.42	2.14	8.98
XI	$CHCl_2CHBrCH_2Cl$	10	60° (5)	1.8463	1.5300	45.26	45.31	16.50	1.76	-
XIII	94% threo- and 6% erithro-$CHClBrCHBrCH_2Cl$	92	74° (2)	2.1318	1.5563	40.87	41.32	-	-	-
XIII	94% erithro and 6% threo-$CHClBrCHBrCH_2Cl$	94	74° (2)	2.1029	1.5590	41.50	41.32	13.52	1.62	-
XV	$CHClBrCF_2CH_2Cl$	48	145°(758)	1.8425	1.4560	33.61	33.35	16.61	1.44	16.37

REFERENCES

1 M. L. Poutsma. J. Am. Chem. Soc., 87, 2171 (1965).

2 M. L. Poutsma, R. L. Hinman. J. Am. Chem. Soc., 86, 3807 (1964)

3 B. L. Dyatkin, E. P. Mochalina, I. L. Knunyants. Uspekhi Khimii, 35, 979 (1966).

4 I. L. Knunyants, L. S. German. Izvest. AN SSSR, Ser. Khim., 1065 (1966).

5 L. S. Boguslavskaya, A. P. Voronin, K. V. Yarovykh, A. P. Sineokov. Zhurnal Org. Khim., 11, 257 (1975).

6 P. B. D. De la Mare and P. Bolton. Electrophilic additions to unsaturated systems, Izd, "Mir", Moscow, 1968.

7 K. Jates, R. C. McDonald. J. Org. Chem., 38, 2465 (1973).

8 R. C. Fahey, C. Schubert. J. Am. Chem. Soc., 87, 8172 (1965).

9 L. S. Boguslavskaya. Uspekhi Khimii, 41, 1591 (1972).

10 J. H. Rolston, K. Jates. J. Am. Chem. Soc., 91, 1469 (1969).

11 R. C. Fahey, H. J. Schneider. J. Am. Chem. Soc., 90, 4429 (1965).

12 M. A. Wilson. Tetrahedron Letters, 1037 (1965).

13 J. Dana, O. Convert, C. Perrin. J. Org. Chem., 40, 2133 (1975).

14 G. Olah. Angew. Chem., 85, 183 (1973).

15 L. S. Boguslavskaya, A. B. Bulovyatova. Zhurnal Org. Khim., 7, 443 (1970).

16 L. S. Boguslavskaya, V. S. Etlis. Zhurnal Org. Khim., 7, 1811 (1971).

17 L. S. Boguslavskaya, V. S. Etlis, K. V. Yarovykh, A. B. Bulovyatova. Zhurnal Org. Khim., 7, 1339 (1971).

18 R. C. Fahey. Topics in stereochemistry, New York, 3, p. 7, 1971.

19 L. J. R. Shelton, L. H. Lee. J. Org. Chem., 24, 1271 (1959).

20 F. M. Lewis, F. R. Mayo, J. Am. Soc., 70, 1533 (1948).

21 Beilst. EIII, 1, 648.

22 A. J. Hill, E. J. Tisher. J. Am. Chem. Soc., 44, 2582 (1922).

23 R. J. Abraham, K. Parry. J. Chem. Soc., 13, 724 (1971).

24 L. F. Hatch, D. W. Mc. Donald. J. Am. Chem. Soc., 74, 2911 (1952).

25 L. S. Boguslavskaya, K. V. Yarovykh, A. B. Bulovyatova. Zhurnal Org. Khim., 3, N11, 1932 (1969).

26 L. S. Boguslavskaya, A. B. Bulovyatova, A. P. Sineokov, V. S. Etlis. Zhurnal Org. Khim., 7, 637 (1971).