REARRANGEMENT OF POLYHALOALKYL RADICALS CONTAINING

FLUORINE IN A TRIHALOMETHYL GROUP

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V. N. Kost, T. T. Vasil'eva, and R. Kh. Freidlina

Institute of Heteroorganic Compounds, Academy of Sciences, USSR Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 300-307, February, 1965 Original article submitted March 26, 1963

In development of work on the rearrangement of free radicals in solution [1, 2] with 1,2-migration of chlorine by the scheme (1)

$$XCCl_{2}\dot{C}YCH_{2}Z \rightarrow X\dot{C}ClCYClCH_{2}Z \tag{1}$$

(in which X = H, Cl, CH₃; Y = H, Cl, Br, CH₃; Z = Cl, Br, CCl₃, SR) it was of interest to study the rearrangement of radicals containing fluorine in a trihalomethyl group, namely FCCl₂CHCH₂Br, FCCl₂CClCH₂Br, FCCl₂CBrCH₂Br, FCCl₂CBrCH₂Br, FCCl₂CClCHCH₂CCl₃, F₂CClCBrCH₂Br, FCCl₂CHCH₂Cl, FCCl₂CClCHCH₂Cl, F₂CClCHCH₂Cl. These radicals were generated: 1) by the free-radical addition of HBr or CCl₃Br to fluorohalopropenes of structure CF_nCl₃-nCY = CH₂, in which Y = H, Cl, Br; n = 1.2; 2) by the action of ultraviolet radiation or benzoyl peroxide on these fluorohalopropenes.

In the first case reaction goes by the scheme (2):

$$HBr \xrightarrow{h_{\nu}} Br$$

$$CH_{2}=CYCCl_{2}F + Br \xrightarrow{\rightarrow} CH_{2}Br\dot{C}YCCl_{2}F (A) \xrightarrow{Rearrangement} CH_{2}BrCYCl\dot{C}ClF (B)$$

$$HBr \downarrow d \qquad HBr \downarrow e$$

$$CH_{2}BrCHYCCl_{2}F \qquad CH_{2}BrCYClGHClF$$

$$(2)$$

The radicals (A) and (B) by reacting with hydrogen bromide give nonrearranged and rearranged addition products.

In the second case under the conditions selected there occurs free-radical chain dimerization, which for the case of monofluorotrihalopropenes may be represented by the scheme (3):

$$CH_{2}=CYCCl_{2}F \xrightarrow{Cl} ClCH_{2}\dot{C}YCFCl_{2} (C) \xrightarrow{Rearrangement} ClCH_{2}CYClCFCl (D)$$

$$c \downarrow CH_{2}=CYCCl_{2}F \qquad (d \downarrow CH_{2}=CYCFCl_{2} (G)$$

$$ClCH_{2}CY (CFCl_{2}) CH_{2}\dot{C}YCFCl_{2} (E) \qquad ClCH_{2}CYClCFClCH_{2}\dot{C}YCFCl_{2} (F)$$

$$ClCH_{2}CY (CFCl_{2}) CH_{2}CY=CFCl + Cl ClCH_{2}CYClCFClCH_{2}CY=CFCl + Cl$$

$$(3)$$

The radicals (C) and (D) are able to add to the original halo olefin with formation of the dimeric radicals (E) and (F), which become stabilized by the loss of halogen atoms, which continue the chain.

Thus, in the first series of experiments rearrangement [stage (c), scheme (2)] competed with substitution [stage (d)], and in the second series rearrangement [stage (b)], scheme (3)] competed with addition [stage (c)].

It should be noted that the presence of fluorine in the trihalomethyl group of the polyhalopropenes studied lowers their reactivities appreciably in radical-type reactions (Table 1). Polyhalopropanes with two fluorine atoms in the trihalomethyl group are particularly inert in the reactions studied.

TABLE 1

Reactants	I nitiation by	Time, h	Total yield of products, %	Reference
$CCl_{3}CH = CH_{2}; HBr$ $FCCl_{2}CH = CH_{2}; HBr$ $FCCl_{2}CCl = CH_{2}; HBr$ $CCl_{3}CBr = CH_{2}; HBr$ $CCl_{3}CBr = CH_{2}; HBr$	UV BZ2O2 UV	2,5 10 10 10 Fast 6 20	88 58 0 100 34	[3] [3] [4] [1] [4]
$CCl_{3}CH = CH_{2}$ $FCCl_{2}CH = CH_{2}$ $F_{2}CCl_{2}CH = CH_{2}$ $F_{2}CClCH = CH_{2}$	Bz₂O₂ UV Ţ	20 8 20 40	40 32 50 21	[5]

*The products are listed in Tables 2 and 3.

		Products					
	Initiation	nonrearranged		rearranged			
Reactants	by	formula	yield, 껴	formula	yield, 🌾	Reference	
$CCl_{s}CH = CH_{s}; HBr$ $FCCl_{s}CH = CH_{s}; HBr$ $FCCl_{s}CBr = CH_{s}; HBr$ $FCCl_{s}CCl = CH_{s}; HBr$ $F_{s}CClCH = CH_{s};$ $CCl_{s}Br$	ÜV # # #	FCCl ₂ CH ₂ CH ₂ Br. FCCl ₂ CHBrCH ₂ Br FCCl ₃ CHBrCH ₂ Br FCCl ₅ CHClCH ₂ Br (F ₂ CClCHBrCH ₂ CCl ₃ F ₂ CClCHCH ₂ CCl ₃ CH ₂ CHBrCF ₂ Cl	39 58 85 67 8	HCCl ₂ CHClCH ₂ Br FCClHCHClCH ₂ Br CFCl=CClCH ₂ Br 	88 18 2,2 — —	[3] [3] [4] —	

In Table 2 we summarize the results on the homolytic addition of HBr to $CCl_3CH = CH_2$ (I), $CFCl_2CH = CH_2$ (II), $CFCl_2CBr = CH_2$ (III), and $CFCl_2CCl = CH_2$ (IV), and of $CBrCl_3$ to $CF_2ClCH = CH_2$ (V) under the action of ultraviolet radiation. The addition of HBr to the first three polyhalopropenes has been described earlier [3, 4]. In the case of (IV) the addition of HBr under the action of ultraviolet radiation or when heated with benzoyl peroxide does not occur, which probably arises from the reversibility of the addition of a bromine atom by the scheme (4):

$$CFCl_2CCl = CH_2 + Br \neq CFCl_2CClCH_2Br$$
(4)

The inertness of the radical formed favors the reverse reaction. It is interesting that the presence of hydrogen bromide inhibits the dimerization of (IV). Thus, whereas in absence of hydrogen bromide this trichlorofluoropropene dimerizes under ultraviolet irradiation to the extent of 70% (Table 3, third example), when HBr is passed the original trichlorofluoropropene can be recovered almost completely. The following mechanism may be proposed for the termination of chain dimerization in accordance with the scheme (5):

$$CFCl_{2}CCl = CH_{2} \xrightarrow{O1} (5)$$

$$CFCl_{2}CClCH_{2}Cl \xrightarrow{HBr} CFCl_{2}CHClCH_{2}Cl + Br$$

As stated, in this case bromine does not continue the chain. We succeeded in bringing about the addition of HBr to (IV) at low temperature (-40°), when we obtained the nonrearranged bromide CFCl₂CHClCH₂Br. In the reaction of trichlorobromomethane with (V) under ultraviolet irradiation we obtained only nonrearranged telomers by the scheme (6):

$$CH_2 = CHCF_2Cl + CBrCl_3 \rightarrow$$

$$\rightarrow CCl_3 [CH_2CH (CF_2Cl)]_n Br; n = 1,2$$
(6)

It will be seen from Table 2 that in addition reactions the yield of rearranged products diminishes on the introduction of one fluorine atom into the trihalomethyl group. (IV) and (V) no longer give rearranged addition products.

			Ρŗ	oductș		
	Initiation	nonrearranged		rearranged		
Starting substance	by (time, h)	formula	yield, %	formula	yield, %	Reference
CCI ₃ CH=CH ₃ FCCI ₃ CH=CH ₂ FCCI ₃ CCI=CH ₂ FCCI ₃ CBr=CH ₂ F ₃ CCICH=CH ₂ F ₃ CCICH=CH ₂	$\begin{array}{c} Bz_2O_2 \left(8\right) \\ UV \\ UV \\ 0 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1$	$CICH_{2}CHCICCI_{3}CH_{3}CH=CCI_{3}$ $CICH_{2}CHCICCI_{3}CH_{3}CH=CFCI$ $CICH_{2}CCI_{3}CFCICH_{3}CCI=CFCI$ $CICH_{2}CCI_{3}CFCICH_{2}CCI=CFCI$ $CFCI=CCICH_{3}Br$ $CF_{3}=CCICH_{3}Br$	3 13 13 4 23		11 ^{,3} 20	[5]

The results obtained in the secon' series of experiments are given in Table 3. As we reported earlier [5], in reaction with benzoyl peroxide (I) gives only a rearranged dimer of structure ClCH₂CHCl ·CCl₂CH₂CH = CCl₂. Under ultraviolet radiation (II) also gives only a rearranged dimer of structure ClCH₂CHClCFClCH₂CH = CFCl.

The presence of halogen on the second carbon atom facilitates the dimerization of (IV) and (III) appreciably. In these cases the dimerization of fluorotrihalopropenes sets in even when the samples are kept in diffuse light with formation of nonrearranged dimers of structure $ClCH_2CCl(CFCl_2)CH_2CCl = CFCl$ and $Bl_CH_2CBr(CFCl_2)$ $\cdot CH_2CCl = CFCl$ respectively. Under ultraviolet radiation dimerization is speeded up, and together with these dimers, products are obtained which are formed by the 1,2-migration of chlorine in the intermediately formed radicals [scheme (3), stage (b)]. In the case of (IV) we isolated a rearranged dimer of structure $ClCH_2CCl_2CFCl$ $\cdot CH_2CCl = CFCl$, and in the case of (III) the rearranged radical (D) [scheme (3), Y = Br] is stabilized by the elimination of a bromine atom with formation of the isomer of structure $CFCl = CClCH_2Br$.

The presence of two fluorine atoms in the trihalomethyl group of the polyhalopropenes studied considerably reduces the ease of dimerization. When (V) was exposed to ultraviolet radiation for 40 h, we obtained only 3.6% of dimer fraction, consisting mainly of nonrearranged dimer.

To prove the structures of the dimers synthesized we developed methods which were in principle as follows. The rearranged dimers, having a normal structure, were converted by hydrolysis and subsequent dehalogenation and hydrogenation into known carboxylic acid derivatives. Nonrearranged dimers, which have a trihalomethyl side group, were converted by hydrolysis into 2-methyleneglutaric acid.

Among the substances studied, polyhalopropenes containing bromine occupy a special place, i.e., $CFCl_2CBr = CH_2$ and $CF_2ClCBr = CH_2(VI)$ (Table 4). In these cases, together with the transformations mentioned, homolytic isomerization in accordance with the scheme (7) occurs:

 $CF_{n}Cl_{3-n}CBr=CH_{2} + Br \rightarrow CF_{n}Cl_{3-n}\dot{C}BrCH_{2}Br (A) \xrightarrow{\text{Rearrangement}} (7)$ $\rightarrow \dot{C}F_{n}Cl_{2-n}CBrClCH_{2}Br (B) \rightarrow CF_{n}Cl_{2-n}=CClCH_{2}Br + Br; \quad n = 0, 1, 2$

The rearrangement of the initially formed radicals (A) leads to the formation of the radicals (B), in which the bromine atom is on the carbon atom adjacent to the radical center. These radicals can become stabilized by the loss of a bromine atom and formation of unsaturated compounds isomeric to the starting compounds.

The tendency for these polyhalopropenes to isomerize falls off sharply as fluorine atoms accumulate in the trihalomethyl group, but it remains appreciable even in the case of (VI). The latter under the conditions given in Table 4, and also when heated to 180° or in presence of benzoyl peroxide at 80° , forms a mixture of products. In all cases we were able to isolate the following from the reaction mixture: the isomerization product, 3-bromo-2-chloro-1,1-difluoropropene (VII), and the dimer, which was assigned the structure BrCH₂CBr(CF₂C1)CH₂CC1 = CF₂ on the basis that under the given

TABLE 4

Starting substance	Initiation by	Time, h	Isomeriza- tion (% of amt. that reacted)	Reference	
$CCl_3CBr = CH_2$ FCCl_2CBr = CH_2 F_2CClCBr = CH_2	UV # #	Fast 6 20	100 34 8	[1] [1]	

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·····		Rearrangement			
tructure of original Structure of rearrang radical		in reactions with HBr, η_o on sum of products	in dimeriza- tion proces- ses, %on sum of products		
BrCH2ĊHCCl3	BrCH ₂ CHClĊCl ₂	~100	_		
BrCH2CHCCl2F	BrCH ₂ CHClĊFCl	30	_		
BrCH ₂ CBrCCl ₃	BrCH ₂ CBrClĊCl ₂		100		
BrCH2CBrCFCl2	BrCH ₂ CBrClCFCl	3	34		
BrCH ₂ ĊBrCF ₂ Cl	$BrCH_2CBrClCF_2$	—	8		
BrCH2ĊClCFCl2	BrCH ₂ CCl ₂ ĊFCl		_		
ClCH2CHCCl3	ClCH ₂ CHClĊCl ₂	-	~100		
ClCH2CHCFCl2	ClCH₂CHClĊFCl	_	~100		
CICH2CHCF2Cl	ClCH ₂ CHClĊF ₂		0		
ClCH2ĊClCFCl2	ClCH ₂ CCl ₂ ĊFCl		15		
			1		

conditions only the nonrearranged radical $BrCH_2CBrCF_2C1$ may give a dimer in further transformations, whereas the radical $BrCH_2CBrClCF_2$ formed as a result of rearrangement is stabilized by the loss of a bromine atom with formation of (VII).

On the basis of the data in Tables 2-4 we compiled Table 5, which characterizes the tendency of the radical studied to undergo rearrangement with 1,2-migration of chlorine.

EXPERIMENTAL*

1. Dimerization of 3,3-dichloro-3-fluoropropene (II). A solution of 40 g of (II) in 40 ml of benzene was irradiated in a quartz ampoule with a PRK-4 lamp for 20 h. By vacuum distillation we isolated 16.5 g (41%) of 1,4,5,6-tetrachloro-1,4-difluoro-1-hexene (VIII); b. p. 69-70° (4 mm); n_D^{20} 1.4745; d_4^{20} 1.4984. The structure of (VIII) was proved as follows. By the hydrolysis of (VIII) with 95% sulfuric acid at 70-80° we obtained 4,5,6-tri-chloro-4-fluorohexanoic acid (IX) in 80% yield; b. p. 140-141° (3 mm); b. p. 90-90.5° (from heptane).

When (IX) was heated with zinc dust in acetic acid (6 h, 110°) we obtained a 32% yield of 4-fluoro-4-hexenoic acid (X) (b. p. 82-83° (3 mm); n_D^{20} 1.4380; d_4^{20} 1.1261) and a 27% yield of 4-oxohexanoic acid; b. p. 113-114° (3 mm); m. p. 37°. The literature [6] gives m. p. 36-37°. The same acid was prepared by the hydrolysis of (X) with 95% sulfuric acid at about 20°. The 2,4-dinitrophenylhydrazones prepared from the two samples of the acid both had m. p. 186-187° alone, and in admixture with the 2,4-dinitrophenylhydrazone of the 4-oxohexanoic acid prepared earlier [5].

2. Addition of hydrogen bromide to 2,3,3-trichloro-3-fluoropropene (IV). (IV) was prepared as described in [7], but in 2-ethoxyethanol. Apart from (IV) we isolated 1,2,3-trichloro-1-fluoropropene in 5% yield; b. p. 124°; n_D^{20} 1.4670; d_4^{20} 1.4965.

^{*}The analyses and molecular refractions of the products are presented in Table 6.

TA	BLE	6

	ò		Fou	nd			Cal	culated	
Formula	Expt. N	С, %	Н, %	F, %	MR	с, %	Н, %	F, %	MR
ClCH ₂ CHClCFClCH ₂ CH=CFCl	1	28,25	2,56	14,63	48,42	27,94	2,34	14,73	48,70
ClCH ₂ CHClCFClCH ₂ CH ₂ COOH	1	30,62	3,39	8,35		30,34	3,39	8,00	;
CH₃CH≕CFCH₂CH₃COOH	1	54,21	5,20 6,73 6,70	14,50	30,80	54,53	6,86	14,38	30,87
CFCl=CClCH ₂ Cl	2	21,93	1,18	14,52 12,18 44,50	30,30	22,05	1,24	11,63	ി,10
CFCl ₂ CHClCH ₂ Br	2	14,53	1,32	8,01	38,32	14,75	1,23	7,77	38,32
ClCH ₂ CCl(CFCl ₂)CH ₂ CCl=CFCl	3	14,39 22,35 22,45	1,29 1,34	11,69	57,86	22,05	1,24	11,63	58,43
ClCH ₂ CCl ₂ CFClCH ₂ CCl=CFCl	3	22,15	1,55	11, 15 10, 55 10, 58	57,65	22,05	1,24	11,63	58,43
ClCH ₂ CCl(CFCl ₂)CH ₂ COOH	3	23,55	1,20 1,83	7,07	46,10	23,28	1,95	7,36	46,19
CICH ₂ CCl(CFCl ₂)CH ₂ COOH	3	36,80	3,62	4,65	—	36,81	3,56	4,48	51257-5
ClCH ₂ CCl(CFCl ₂)CH ₂ CCl ₂ COOH	3	20,88	1,33	5,42	-	21,14	1,48	5,57	
$ClCH_2CH(CF_2Cl)CH_2CH=CF_2$	4	31,86	2,73	34,00	38,81	32,02	2,68	33,78	38,76
CF2ClCHBrCH2CCl3	5	15,48	1,08	11,78	47,53	15,46	0,97	12,03	47,69
$CF_2ClCH(CH_2CHBrCF_2Cl)CH_2CCl_3$	5	20,09	1,47	17,60	66,07	19,86	1,43	17,95	66,21
CF2ClCH=CHCOOH	5	31,03	1,92	23,76		30 ,7 0	1,93	24,28	
HOOCCH(CH2CHBrCF2Cl)CH2COOH	5	27,11	2,58	12,00	_	27,16	2,60	12,28	
$CF_2 = CClCH_2Br$	6	18,69	0,99	19,21	27,80	18,83	1,05	19,41	28,01
$BrCH_2CBr(CF_2Cl)CH_2CCl==CF_2$	6	18,36	1,02	18,86	53,38	18,82	1,05	19,41	54,29

A solution of 4 g of (IV) and 5 g of hydrogen bromide in heptane was irradiated in a quartz apparatus with ultraviolet radiation (2 h, -40°). By vacuum distillation we obtained 5.1 g (85%) of 3-bromo-1,1,2-trichloro-1-fluoropropane; b. p. 71-72° (2 mm); n_D^{20} 1.4909; d_4^{20} 1.8461. The structure of this bromotrichlorofluoropropane was proved by its dehydrobromination to (IV).

3. Dimerization of 2,3,3-trichloro-3-fluoropropene (IV). a) When a sample of (IV) was kept for two months at about 20° in diffused light and then distilled we isolated a 28% yield of 1,2,4,5,5-pentachloro-4-(chloromethyl)-1,5-difluoro-1-pentene (XI); b. p. 100° (3 mm); n_D^{20} 1.5040; d_4^{20} 1.6727. b) Under the conditions of expt. 1 (without solvent) from 10 g of (IV) by vacuum distillation we isolated two dimers: (XI) (5.8 g, 58% yield; b. p. 100° (3 mm); n_D^{20} 1.5030; d_4^{20} 1.6740) and 1,2,4,5,5,6-hexachloro-1,4-difluoro-1-hexene (1.2 g, 12% yield; b. p. 119-120° (2 mm); n_D^{20} 1.5110; d_4^{20} 1.6989.

The structure of (XI) was proved as follows. By the action of nitric acid (sp.gr. 1.51) on (XI) (60-70°, 1.5 h) we obtained two acids: 3,4,4-trichloro-3-(chloromethyl)-4-fluorobutyric acid (XII) (54% yield); b. p. 122-123° (2 mm); n_D^{20} 1.5010; d_4^{20} 1.6481; benzylisothiuronium salt, m. p. 111-112° (from water). 2,2,4,5,5-Pentachloro-4- (chloromethyl)-5-fluoropentanoic acid (26% yield); m. p. 101-102° (from heptane). (XII) was heated with zinc dust in acetic acid (2 h, 90°), after which the reaction product, without isolation in the pure state, was hydrogenated over freshly reduced Pd/BaSO₄ in methanol saturated with ammonia at about 20°. We obtained isovaleric acid; b. p. 76-78° (15 mm); n_D^{20} 1.4040; d_4^{20} 0.9459. The benzylisothiuronium salt had m. p. 144-145° (from water), undepressed by admixture of the benzylisothiuronium salt prepared from known isovaleric acid.

4. Dimerization of 3-chloro-3,3-difluoropropene (V). From 11 g of (V) under the conditions of expt. 1 (without solvent) in the course of 40 h we obtained, after distilling off unchanged chlorodifluoropropene, 2.3 g of residue (21% conversion), from which we isolated 0.4 g (3.6%) of 5-chloro-4-(chloromethyl)-1,1,5,5-tetrafluoro-1-pentene (XIII); b. p. 86-87° (15 mm); n_D^{20} 1.4100; d_4^{20} 1.4365.

The structure of (XIII) was proved by hydrolysis with 95% sulfuric acid at 130-140° into 2-methyleneglutaric acid, m. p. 130°, undepressed by admixture of the 2-methyleneglutaric acid prepared earlier [8].

5. Addition of bromotrichloromethane to 3-chloro-3,3-difluoropropene (V). A solution of 20 g of (V) in 70 g of bromotrichloromethane was irradiated in a quartz ampoule with a PRK-4 lamp for 20 h. By vacuum distillation we isolated 2-bromo-1,4,4,4-tetrachloro-1,1-difluorobutane (XIV) (37 g, 67% yield; b. p. 73-74° (10 mm); n_D^{20} 1.4803; d_4^{20} 1.8583) and 2-bromo-1,6,6,6-tetrachloro-4-(chlorodifluoromethyl)-1,1-difluorohexane (XV) (6 g, 8% yield; b. p. 99-100° (3 mm); n_D^{20} 1.4710; d_4^{20} 1.7908).

The structure of (XIV) was proved as follows. By the reaction of 17 g of (XIV) with 8 g of diethylamine in methanol (24 h, 20°) we obtained 6.7 g (53%) of 1,4,4,4-tetrachloro-1,1-difluoro-2-butene (XVI); b. p. 71-72° (65 mm); n_D^{20} 1.4490; d_4^{20} 1.5249.

By the ozonization of (XVI) we obtained chloral, identified as the 2,4-dinitrophenylhydrazone of methyl glyoxylate [9]. By the hydrolysis of (XVI) with 94% sulfuric acid (80-85°, 2.5 h) we obtained chlorodifluorocrotonic acid in 60% yield [b. p. 84-85/15 mm and m. p. 34-35° (from petroleum ether)] and fumaric acid in 8% yield (m. p. 286°).

To prove the structure of (XV) we hydrolyzed it with 95% sulfuric acid at 140-150°. We obtained 2-(2-bromo-1-chloro-1,1-difluoropropyl)succinic acid, m. p. 142-143°, in 40% yield.

6. Isomerization of 2-bromo-3-chloro-3,3-difluoropropene (VI). 15 g of (VI) was exposed to ultraviolet radiation in a quartz ampoule for 20 h. By the distillation of the combined products from three experiments we isolated, apart from unchanged bromochlorodifluoropropene (27 g, i.e., 60% of the amount taken), 3-bromo-2-chloro-1,1-difluoropropene (VII) (1.4 g, 3% yield; b. p. 80° (60 mm); n_D^{20} 1.4588; d_4^{20} 1.8806) and 4-bromo-4-(bromomethyl)-2,5dichloro-1,1,5,5-tetrafluoro-1-pentene (5.2 g, 11% yield; b. p. 112-113° (1 mm); n_D^{20} 1.5000; d_4^{20} 2.1095.

To prove the structure of (VII) by its reaction with diethylamine in ether we converted it into 2-chloro-N,N-diethyl-3,3-difluoroallylamine; b. p. 68° (70 mm); n_D^{20} 1.4130; d_4^{20} 1.0890. Picrate, m. p. 95°. The literature [10] gives: b. p. 67-68° (70 mm); n_D^{20} 1.4120; d_4^{20} 1.0884; picrate, m. p. 94-95°.

SUMMARY

A study was made of the free-radical addition, dimerization, and isomerization reactions of polyhalopropenes containing fluorine in the trihalomethyl group. The introduction of a fluorine atom into the trihalomethyl group lowers the reactivity of polyhalopropenes in reactions of the radical type, as compared with the corresponding polychloropropenes.

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