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VINYLIC HALOGEN EXCHANGE REACTIONS IN 1,2-DIHALOPERFLUOROCYCLOALKENES

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SUMMARY

A variety of 1,2-dihaloperfluorocycloalkenes bearing chlorine, bromine or iodine at the vinylic positions have been synthesized by two different halogen exchange reactions. A novel exchange of vinylic chlorine by hydrogen bromide occurred with a catalyst composed of calcium sulfate and activated charcoal. At 220–280° the yield of 1-bromo-2-chloro- and 1,2-dibromo-perfluorocycloalkenes was 70–95% based on recovered starting material. No addition nor allylic substitution products were found. Metal halide exchange reactions were very slow in low polarity aprotic solvents, but proceeded quickly and in good yields in high polarity aprotic solvents such as dimethylformamide and hexamethylphosphoramide. The observed order of reactivity toward I^- was 1,2-dichloroperfluoro-cyclobutene $>$ cyclopentene $>>$ cyclohexene. Displacement of vinylic fluorine by halide ion was not observed.

INTRODUCTION

Previous studies on vinylic halogen exchange reactions in 1,2-dihaloperfluorocycloalkenes have been limited to the displacement of vinylic chlorine by fluoride[1,2]. Synthesis of compounds bearing vinylic bromine or iodine have been previously achieved by the reaction of Br_2 or I_2 with perfluorocycloalkenyl Grignard and lithium reagents[3,4] or by a novel reaction of HBr with 1,2-dichloroperfluorocyclopentene over a $BaSO_4$/C catalyst to yield 1-bromo-2-chloro- and 1,2-dibromo-perfluorocyclopentene[5].

Because of our need to obtain various 1,2-dihaloperfluorocycloalkenes, we have undertaken a study of the halide exchange with several readily available

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starting materials, namely 1,2-dichloroperfluorocyclobutene (I), 1,2-dichloroperfluorocyclopentene (II), 1,2-dichloroperfluorocyclohexene (III) and perfluorocyclohexene (IV).

RESULTS AND DISCUSSION

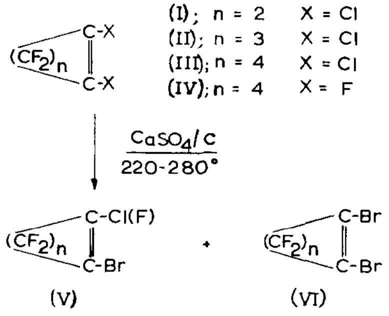
We have re-investigated the catalytic exchange of vinylic chlorine by HBr and found that a catalyst composed of a 75/25 wt.% activated charcoal and calcium sulfate is superior to that reported previously[5]. In a typical run, the 1,2-dichloroperfluorocycloalkene and a three-fold excess of hydrogen bromide were passed slowly through the catalyst at 220–280°. Table 1 contains the results of these experiments.

TABLE 1

PRODUCT DISTRIBUTION FROM THE CATALYTIC HBr EXCHANGE WITH 1,2-DIHALOPERFLUOROCYCLOALKENES

Olefin	% Yield (V)	% Yield (VI)	Total Yield[a]
(I)	25.4	39.2	92.4
(II)[b]	21.7	15.4	82.3
(III)	30.1	21.5	73.5
(IV)	trace	trace	trace

[a] Yield based on recovered starting material.
[b] Catalyst was $BaSO_4/C$ in 25/75 wt.% ratio.



It is interesting to note that under the conditions employed in these experiments no products resulting from hydrogen bromide addition to the double bond nor loss of fluorine due to allylic substitution were found. Earlier reports from these laboratories have shown that under similar reaction conditions perfluoroalkenes and perfluorocyclobutene gave only the hydrogen bromide adduct[6]. At higher temperatures (390°) hydrogen chloride over a charcoal catalyst is reported to yield both vinylic and allylic substitution[7].

The method of choice for the preparation of perfluorocycloalkenes bearing vinylic iodine proved to be the nucleophilic displacement of vinylic chlorine or bromine by iodide ion. Initially, we explored the use of low polarity aprotic solvents such as acetone and "diglyme" [di-(2-methoxyethyl)ether] since the apparent order of nucleophilicity of halide ions in these solvents is $I^- > Br^- > Cl^-$ [8]. Although some products containing vinylic iodine were obtained the rates of these reactions were prohibitively slow. The results from some of our experiments using low polarity aprotic solvents are summarized in Table 2.

TABLE 2

HALIDE ION EXCHANGE WITH 1,2-DIHALOPERFLUOROCYCLOALKENES IN LOW POLARITY SOLVENTS

Olefin	Salt	Molar Ratio[a]	Solvent[b]	°C[c]	Time (h)	Yield % Mono-subst.	Yield % Di-subst.
(I)	LiBr	1.0	A	R	56	47	trace
(IV)	LiBr	4.0	C	95[d]	134	—	—
(I)	KI	2.5	A	95[d]	120	46	16
(II)	KI	2.5	D	R	168	7.4	—
(IV)	NaI	9.0	A	R	168	—	—

[a] Molar ratio salt/olefin.
[b] Solvent A = acetone, D = diglyme, C = 80% acetone, 20% DMF.
[c] Temperature R = reflux.
[d] Reaction carried out in sealed Carius tube.

The relatively poor conversions, especially with increasing ring size, and the extremely long reaction times forced us to look for modifications of the reaction parameters which would increase conversion yields and minimize reaction times. An increasing amount of evidence suggested that the initial halide ion attack to form a carbanion stabilized by adjacent CF_2 groups was a reversible process, and thus subject to equilibrium conditions. A second possible modification was evident from the elegant work of Winstein *et al.*[9] who proposed that ion-pairing in low polarity solvents leads to significant loss of nucleophilic character of the attacking ion species. On the basis of these data we turned to more polar solvents and increased the ratio of reactants to favor product formation. The results of these experiments are summarized in Table 3.

Several pertinent facts became apparent from these experiments. First of all, a dramatic decrease in reactivity is observed as the ring size is increased. Secondly, the heavier vinylic halogen atoms are more easily displaced by iodide while the vinylic fluorine atom was virtually unreactive under all conditions employed here. And finally, there is an obvious preference for potassium salts rather than lithium salts due to the extensive by-product and tar formation with the latter salt.

At this time, we are unable to explain the large amounts of dimethylamino substituted products which were formed in reactions employing hexamethylphosphoramide as solvent. Since only trace amounts of these unwanted by-products were formed when potassium iodide was used, we suspect that the potassium bromide caused some decomposition of the hexamethylphosphoramide. This may have been due to more basic bromide ion or an impurity in the salt.

TABLE 3

HALIDE ION EXCHANGE WITH 1,2-DIHALOPERFLUOROCYCLOALKENES IN HIGH POLARITY SOLVENTS

						Yield %	
Olefin	Salt	Molar Ratio[a]	Solvent[b]	°C[c]	Time (h)	Mono-subst.	Di-subst.
(I)	KI	2.0	B	R	5	36	26
(I)	KI	4.0	B	65–95	23	10	58
(II)	KI	2.1	B	R	19	45	—
(II)	KI	4.0	B	91–125	20	23	51
(III)	KI	2.0	B	R	134	9	—
(III)	KI	4.0	H	45–135	15	26	—
(IV)	KI	2.0	B	95	88	—	—
(III)[d]	KI	3.0	B	R	30	56[e]	—
(III)[f]	KI	3.0	B	R	34	52	7
(I)	KF	1.0	B	49	48	14	—
(IV)	KCl	6.0	B	95	7 days	—	—
(II)	KBr	4.0	H	65–100	9 days	63[g]	—
(III)	KBr	7.0	H	135	10	3	[h]
(II)	LiI	4.0	B	135	7 days	8	tars

[a] Molar ratio, salt/olefin.

[b] Solvent, B = dimethylformamide, H = hexamethylphosphoramide.

[c] Temperature, R = reflux.

[d] = 1-bromo-2-chloro-(III).

[e] = 1-chloro-2-iodo-(III).

[f] = 1,2-dibromo-(III).

[g] = 1-chloro-2-dimethylamino-(II).

[h] = 54% yield of 1-chloro-2-dimethylamino-(III) and a 9% yield of 1-bromo-2-dimethylamino-(III) was obtained.

EXPERIMENTAL

Elemental analysis were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. and Huffman Laboratories, Inc., Wheatridge, Colo. Infrared spectra were taken on a Perkin–Elmer 337 instrument.

Preparation of 1-bromo-2-chloro- and 1,2-dibromo-perfluorocycloalkenes

A mixture of a 75/25 wt.% activated charcoal–calcium sulfate (4–8 mesh) was added to a 100 cm × 2.5 cm Pyrex glass tube, then slowly heated to approximately 200° under high vacuum. After purging the catalyst with hydrogen bromide, a 3/1 mixture of HBr and the 1,2-dichloroperfluorocycloalkene was introduced into the catalyst bed at 220–280°. The crude reaction product was condensed by two traps in series which were cooled by a salt–ice water mixture. After washing the crude product with aqueous sodium bicarbonate, it was dried ($CaCl_2$) and then fractionally distilled. The physical properties of products obtained are summarized in Table 4.

TABLE 4

PHYSICAL PROPERTIES OF 1-BROMO-2-CHLORO- AND 1,2-DIBROMO-PERFLUOROCYCLOALKENES

Olefin	n	B.p., °C/mm Hg	n_D (°C)	ν(C = C)
(V)	2[a]	81/630	1.3966(25)	1605
(V)	3[b]	101/629	1.3890(25)	1610
(V)	4[c]	122/631	1.3865(27)	1620
(VI)	2[a]	96/630	1.4222(25)	1600
(VI)	3[b]	119/629	1.4213(27)	1605
(VI)	4[d]	140/631	1.4063(27)	1610

[a] Lit.[3], (V), b.p. 79.4(626), n_D^{25} 1.3966; (VI), b.p. 95–96(626).
[b] Lit.[5], (V), b.p. 101(629); (VI), b.p. 119(629).
[c] Lit.[4], b.p. 122(630), n_D^{27} 1.3901(27), ν(C = C) 1620.
[d] Lit.[10], b.p. 149–150, ν(C = C) 1610.

Reaction of 1,2-dihaloperfluorocycloalkenes with metal halides in polar aprotic solvents

The metal salts were finely ground then dried at 150° for 1–2 h. This process was repeated several times. All solvents except the hexamethylphosphoramide were used directly from reagent grade bottles. The reagent grade hexamethylphosphoramide was fractionally distilled and a center fraction used in these experiments.

The metal salt (0.20 mole), 1,2-dihaloperfluorocycloalkene (0.05–0.20 mole) and 100 ml of solvent were stirred and heated for the period specified in Table 3. The reaction mixture was either poured into water and extracted with methylene chloride or steam-distilled and the water distillate extracted with methylene chloride. The methylene chloride product mixture was dried ($CaCl_2$) and then fractionally distilled. It was usually necessary to wash the distilled products carefully to remove all traces of DMF. The physical properties of the compounds prepared by this procedure are summarized in Table 5.

ACKNOWLEDGEMENTS

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TABLE 5

PROPERTIES OF VARIOUS 1,2-DIHALOPERFLUOROCYCLOALKENES

Olefin			B.p.°C/mm Hg	n_D (°C)	ν(C = C), cm^{-1}	% C		% F		% I		% Cl	
						Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
Perfluorocyclobutene													
1-	2-												
Cl	I[a]		54/100	1.4404(29)	1580								
I	I	nc[l]	95/100	1.5110(26)	1550	[b]				67.17	67.00		
Perfluorocyclopentene													
1-	2-												
Cl	I[c]		62/100	1.4272(29)	1600								
I	I	nc	82/100	1.4930(29)	1560	14.03	14.28	26.64	26.16	59.32	58.93		
Br	I	nc	142/628	1.4488(28)	1590	15.75	15.63	29.90	30.15	33.32	32.98	21.00	21.20[d]
Cl	$N(CH_3)_2$	nc	81/15	1.4216(28)	1644	33.15	32.95	44.96	44.71	2.39	2.55[e]	5.53	6.17[f]
Perfluorocyclohexene													
1-	2-												
Cl	I[g]		142/630	1.4213(26)	1605								
I	I	nc	182/629	[h]	1580	15.08	14.87	31.81	31.67	53.11	52.98		
Br	I	nc	166/629	1.4416(27)	1600	16.72	16.79	35.28	35.00	29.45	29.19	18.47	18.25[d]
Cl	$N(CH_3)_2$	nc	[i]	1.4010(29)	1616	[j]							
Br	$N(CH_3)_2$	nc	[i]	1.4175(29)	1610	[k]							

[a] Lit.[4], b.p. 110/630, n_D^{25} 1.4420.

[b] Mass spectrum peaks (rel. intensity) 378(100), 251(13), 124(36).

[c] Lit.[4], b.p. 128/628, n_D^{28} 1.4268.

[d] Bromine analysis.

[e] Hydrogen analysis.

[f] Nitrogen analysis.

[g] Lit.[4], b.p. 144/632, n_D^{26} 1.4218.

[h] M.p. 32°.

[i] Isolated by preparative VPC.

[j] Mass spectrum peaks (rel. intensity) 305(20), 303(50), 268(100), 69(20) and 42(60).

[k] Mass spectrum peaks (rel. intensity) 349(30), 347(30), 268(100), 69(10) and 42(40).

[l] New compound.

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