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FREE-RADICAL REACTIONS OF SILANES WITH 1,2-DIHALOPOLYFLUOROCYCLOALKENES

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SUMMARY

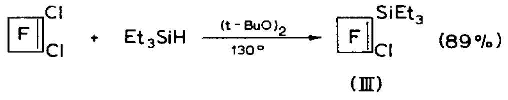
The free-radical reactions of triethylsilane with 1,2-dichloropolyfluorocycloalkenes gave substitution, addition and reduction products. Under similar conditions, 1,2-dibromo- and 1,2-di-iodo-polyfluorocycloalkenes were reduced.

INTRODUCTION

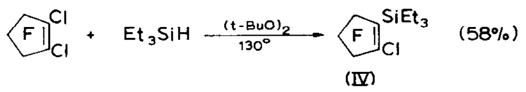
Among the numerous literature reports of free-radical hydrosilylation of alkenes, only three such studies have dealt with cyclic polyfluoro-olefins[1a–c]. These studies were concerned with olefins containing vinylic chlorine and fluorine.

RESULTS AND DISCUSSION

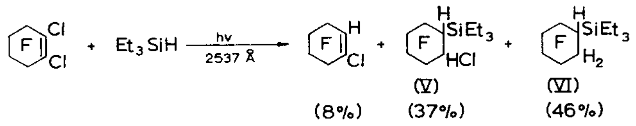
We have investigated the liquid-phase, free-radical reactions of Et_3SiH with four-, five- and six-membered 1,2-dihalopolyfluorocycloalkenes containing vinylic chlorine, bromine and iodine. Part of these results are shown in equations (1)–(3).



(1)



(2)



(3)

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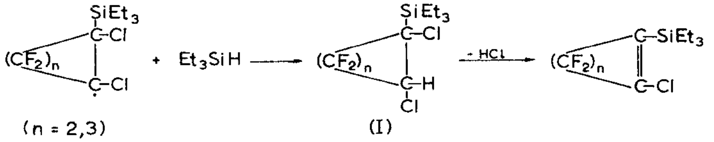
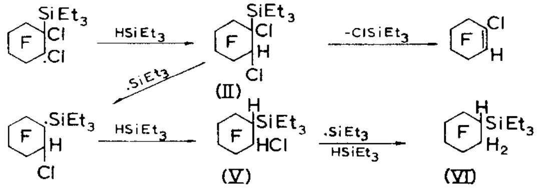
An addition–elimination mechanism is proposed for the four- and five-membered rings,



while a reduction process appears to dominate in the cyclohexenyl derivative:

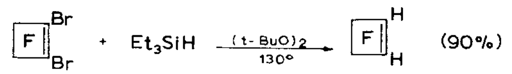


These proposed pathways are not necessarily unique. Silanes are known to add predominately *trans* to olefins under free-radical conditions[2]. Addition–elimination mechanisms[1a, 3], as well as silane reduction of chloroalkanes[4, 5], are well established. The surprising feature is the anomalous behavior of the cyclohexenyl derivative toward triethylsilane. In order to explain this, several things must be considered. As expected, the four-membered ring was more reactive than the five-membered ring toward Et_3SiH. With cyclobutene, more ring strain is relieved when the transient intermediate, (I), is formed. However, once formed, new steric problems develop. Repulsive non-bonded interactions and bond eclipsing between adjacent sp^3-hybridized carbons are present[6]. Unimolecular β-elimination of HCl from (I) relieves this crowding.

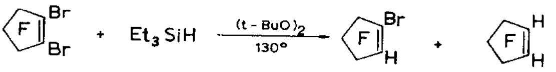
The preponderance of reduction products in the cyclohexenyl derivative can be attributed to dihedral angles. In order to eliminate HCl in a *cis*, unimolecular manner (4-center transition state) from (I) or (II), the hydrogen and chlorine of the ring must be co-planar. The four- and five-membered rings, with a smaller dihedral angle, require less twisting than (II) in order to align the hydrogen and chlorine atoms. (This can be easily verified with the use of molecular models.) Thus, instead of eliminating HCl, the cyclohexyl intermediate, (II), is preferably reduced.

We have found that triethylsilane reduces the vinylic bromine and iodine atoms in polyfluoro-cyclobutenes and -cyclopentenes. The products are thought to be formed by direct bromine abstraction in the same manner that organotin hydrides reduce vinylic and phenyl bromines.

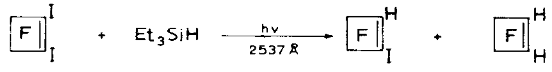
This is the first reported example of vinylic bromine (or iodine) reduction with an alkylsilane under such mild conditions. (All peroxide-initiated reactions were carried out in Fischer–Porter tubes under nitrogen, at 130°.)



(VIII)



(IX) (58%) (X) (35%)



(VII) (VIII)

Those fluoro-olefins, whose physical and spectral data are not recorded, are known compounds and were identified by comparison with authentic samples (Table 1).

EXPERIMENTAL

General reaction procedure

For a typical reaction, under thermal conditions, the triethylsilane (*ca.* 0.10 mole) and 1,2-dihalopolyfluorocycloalkene (0.0330–0.036 mole) along with six drops of t-butyl peroxide were placed in a 100-ml Fischer–Porter tube. The tube was flushed with nitrogen gas, sealed and heated (130–135°) for 22–23 h. After the heating period, the product mixture was analyzed with GLC. An Aerograph "Autoprep" Model A-700 was used for both analytical and preparative purposes.

Yields were determined by gas chromatographic analysis and were based on fluorine-containing compounds.

ACKNOWLEDGMENTS

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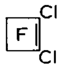
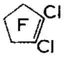
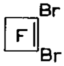
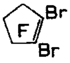
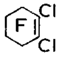
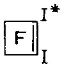
TABLE 1

REACTIONS OF SILANES WITH 1,2-DIHALOPOLYFLUOROCYCLOALKENES

Reactant	mole	Triethyl-silane (mole)	Compound	% Theory	B.p.°C/mm Hg	n_D	(°C)	IR (neat) cm^{-1}
	0.036	0.108	III (nc)	89	192/628	1.4198	(25)	2940(m), 2875(m), 1570(sh), 1330(s), 1240(s), 1120(s), 852(s)
	0.037	0.108	IV (nc)	58	207/619	1.4144	(24)	2940(s), 2875(s), 1585(sh), 1330(s), 1275(s), 1220(s), 1195(s), 1145(s), 1000(s), 875(s), 768(m)
	0.036	1.108	VII	90				
	0.033	0.099	IX X	58 35				
			V	37	243/628	1.4117	(23)	2930(m), 2840(m), 1355(m), 1305(m), 1210(s), 1170(s), 1055(s), 1010(s), 945(s), 825(m), 788(m)
	0.031	0.108	VI (nc)	46	220/628	1.3962	(24)	2950(m), 2880(m), 1355(m), 1305(m), 1200(s), 1165(s), 1055(s), 1030(s), 1000(s), 953(s), 885(m), 780(m)
			XI	8	102/629			
	0.032	0.064	VII (nc) VIII	39 5		1.4281	(27.5)	3110(w), 3050(w), 1545(sh), 1320(s), 1270(s), 1120(s), 1060(s), 860(m), 807(s), 738(s)

* UV radiation study in a Rayonet photochemical reactor.

NMR (TMS std.) τ	GLC column	(°C)	Calcd. %				Found.[7] %			
			C	H	F	Cl	C	H	F	Cl
9.02(m)	4.5 m × 6.4 mm Carbowax	(170)	43.71	5.50	27.66		43.91	5.42	27.38	
9.02(m)	4.5 m × 6.4 mm Carbowax	(158)	40.68	4.66			40.46	4.80		
9.02(m)	4.5 m × 6.4 mm Carbowax	(158)								
	4.5 m × 6.4 mm Carbowax	(105)								
5.67(m), 7.72(m), 9.01(m)	4.5 m × 6.4 mm SE-30	(205)	38.25	4.55		9.41	38.07	4.42		9.49
7.90(m, 3H), 9.07(m, 15H)			42.10	5.29	44.39		42.27	5.36	44.12	
2.72(t of m)			19.06	0.40	30.16		19.10	0.53	30.12	

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7 All compounds analyzed correctly for C, H and F.