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Chlorination of oximes in hydrogen fluoride: formation of *gem*-dihalogenoalkanes

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Abstract

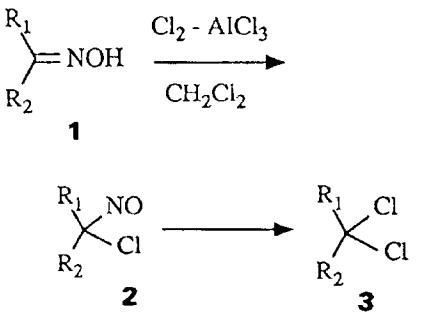
The action of chlorine on oximes in hydrogen fluoride as a medium gives *gem*-dihalogenoalkanes. The reaction proceeds through the intermediate formation of *gem*-chloronitrosoalkanes. The relative proportions between *gem*-dichloro, -difluoro and -fluorochloro compounds are dependent on the presence of a cosolvent. The use of other oxidants, such as nitric oxide, dinitrogen tetroxide or nitrosyl chloride, gives similar compounds.

Keywords: Chlorination, Oximes; Hydrogen fluoride; Dihalogenoalkanes; NMR spectroscopy, Mass spectrometry

1. Introduction

The formation of *gem*-dihalogenoalkanes has been an important goal recently, because of their potential biochemical properties and the requirement for chlorofluorocarbon substitutes [1]. Equally, *gem*-dihalogenocyclohexanes have been proposed as intermediates for the preparation of fluoroaromatic compounds [2,3]. Numerous methods have been developed for their preparation. Besides the complete formation of the carbon skeleton [2,4], other methods have involved transformation of bis-*gem*-trifluoroacetoxy [3] or chloro compounds [2,5–7] by hydrogen fluoride or silver tetrafluoroborate. More specifically, *gem*-difluoroalkanes have been prepared from ketones with toxic reagents such as fluorophosgene [8], sulfur tetrafluoride [9] or its derivative DAST [10,11] and molybdenum hexafluoride [12]. Very recently, this transformation has been performed with dibromodifluoromethane and zinc, generally using a large excess of ketone [13]. Conversions of hydrazones [14–16], oximes [15], diazo compounds [17,18] and thioketals [19–21] have used fluorine or fluoride species in an oxidative medium.

In a preliminary note [22], we reported the easy transformation of simple oximes to *gem*-dichloroalkanes by the action of chlorine in the presence of a Lewis acid (Scheme 1). As we pointed out, the reaction of oximes with anhydrous hydrogen fluoride [23], sulfuric acid or halogenating agents such as phosphorus pentachloride or thionyl chloride [24], usually leads to substituted amines through a Beckmann rearrangement; however, the temperature is an important factor, owing to the different migration aptitudes of the various alkyl or aryl groups [25,26]. At a lower temperature, the reaction gave *gem*-chloronitrosoalkanes when oximes were treated with chlorine in an acidic medium such as hydrochloric acid [27] or in neutral conditions in various solvents [28–30]. The action of hydrogen chloride on these *gem*-chloronitrosoalkanes has been studied [31]; the starting compound was recovered with inversion of configuration, but no exchange of the nitroso group with the halogen atom was observed. Other acidic treatments led to the starting oximes and ketones. Only in the case of perfluoronitrosoalkanes did a radical exchange occur spontaneously with chlorine, leading to chloroperfluoroalkanes [32]. The formation of *gem*-dichloroalkanes from *gem*-chloronitrosoalkanes by randomisation of the functional groups requires photo-



Scheme 1.

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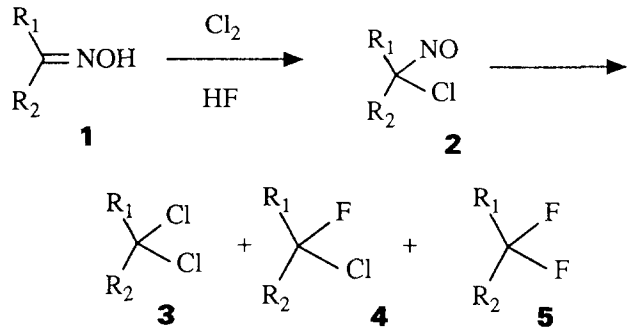


Scheme 2.

chemical activation [33]. Transformation of oximes, or their *gem*-chloronitroso derivatives, into *gem*-dichloroalkanes by the action of hypochlorous acid was limited to the adamantane series [34].

In our preparation of *gem*-dichloroalkanes (Scheme 1) [22], we noted the characteristic blue colour of nitroso derivatives. We interpreted *gem*-dichloroalkane formation as a Lewis acid-mediated substitution of the nitroso group with the chloride anion. When the Lewis acid was replaced by anhydrous hydrogen fluoride, fluorohalogenation of the oximes was observed (Scheme 2) [35].

2. Results

2.1. Two-step procedure

The *gem*-chloronitrosoalkanes **2** were prepared by chlorination of the oximes **1** in diethyl ether [33] (Scheme 3). Relatively pure products were obtained as shown by ^{13}C NMR spectroscopy (see Table 2). Initially, the deep blue *gem*-chloronitrosoalkane was added into neat anhydrous hydrogen fluoride (**caution: see Ref. [36]**). An exothermic reaction occurred and the deep blue colour vanished immediately. After hydrolysis, neutralisation and extraction, various *gem*-dihalogenoalkanes **3–5** were isolated (Scheme 3). Ketones and oximes arising from the hydrolysis of *gem*-chloronitrosoalkane were also formed [31,37]. In the first experiment with cyclohexanone-oxime (**1a**), the products were purified by GLC; difluorocyclohexane (**5a**) (20%), a small amount of dichlorocyclohexane (**3a**), a trace of phenol and cyclohexanone (30%) were obtained. After basic extraction, cyclohexanone-oxime (**1a**) (30%) was recovered (Table 1, entry 1). Addition of methylene chloride as cosolvent to liquid hydrogen fluoride increased the yield of **5a** to 50%.

This reaction was observed with primary and secondary dialkyl ketone derivatives (Table 1). As pointed out by Kosinski [29], *gem*-chloronitrosoalkanes are usually formed when at least one hydrogen is present α to the oxime function.

2.2. One-step procedure

In order to simplify our procedure, we studied the direct chlorination of the oxime in liquid hydrogen fluoride. This allowed ready control of the rate of addition of the oxidant, and hence the temperature of the reaction. We used diethyl ether or ethanol as a cosolvent in all these reactions. However, some of the ethanol reacted to give chloroacetaldehyde diethyl acetal. Under these conditions, the *gem*-chlorofluoro- (**4**) and -dichloroalkanes (**3**) were the main products. Indeed, during this one-step procedure, a chloride anion was released in the medium during the formation of the intermediate *gem*-chloronitroso derivative (Scheme 4); consequently, the concentration of this anion in the medium was important and the proportion of **3** increased as the chloride anion concentration increased.

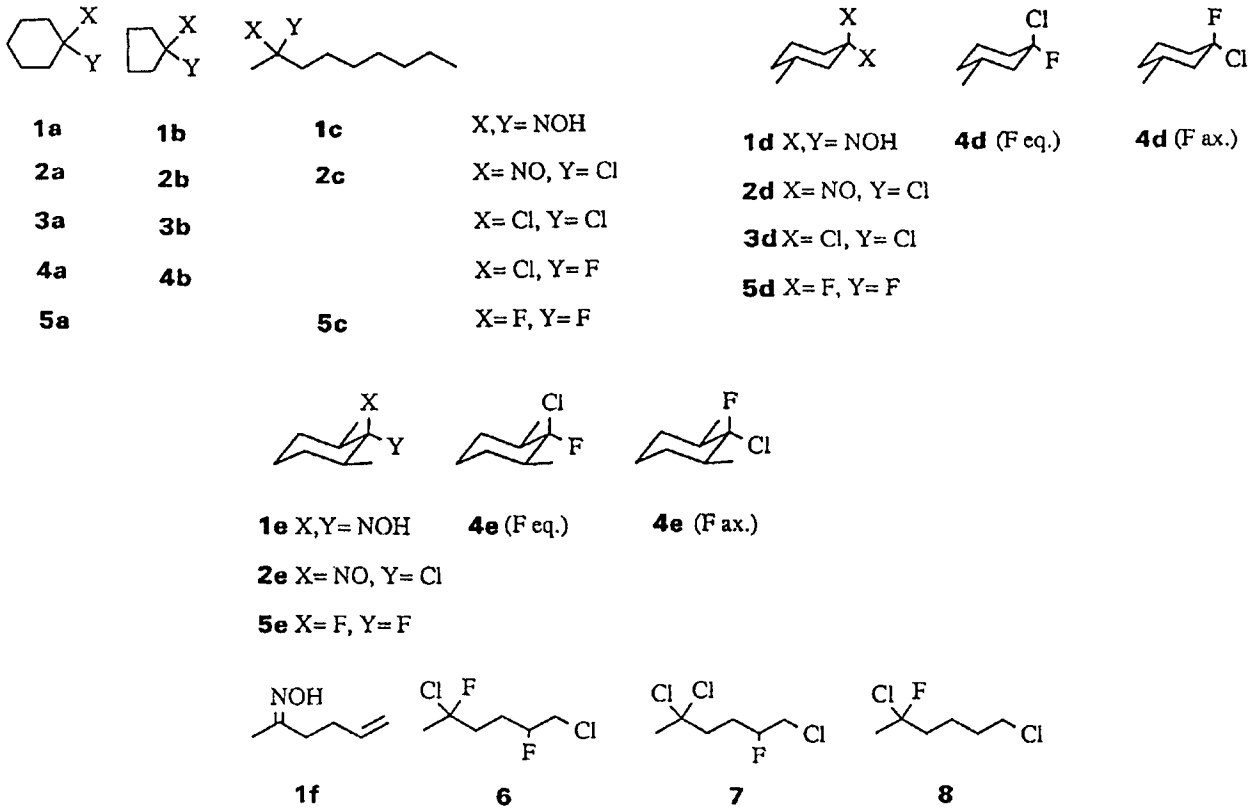
3. Discussion

We tried to observe the cyclisation of a possible chlorocarbo cation intermediate (Scheme 4) in the case of hex-5-en-2-one-oxime (**1f**): unfortunately, as in the case of the benzylacetone-oxime [22], we noticed the halogenation of the unsaturated substituent in addition to *gem*-dihalogenation of the oxime moiety leading to the formation of compounds **6**, **7** and **8**. This experiment was not definitive because this kind of cation could be poorly reactive and the double bond halogenated before its possible alkylation.

We then examined the isomer ratios of the dihalides obtained from methyl cyclohexanone-oximes (Table 1, entries 13 and 15) (Scheme 5). The first example was not conclusive because a 52:48 mixture of **4d** was obtained from a 60:40 mixture of **2d**. The second example was clearer: 1-chloro-1-nitroso-2,6-dimethylcyclohexane (**2e**) was prepared as the sole pure isomer, even if its configuration was not known. From this single compound, a 60:40 mixture of the fluorochloride **4e** was obtained, the major isomer having the fluorine atom *cis* to the methyl groups as shown by NMR spectroscopy. It appears that substitution of the nitroso group is not stereospecific. This observation is compatible with the intermediate formation of a chlorocarbo cation.

It seems that exchange of the nitroso substituent by a fluoride anion needs the presence of a strong acid to protonate or coordinate the initial functional group at the nitrogen or at the oxygen atom. The electron-deficient species so formed could behave as a leaving group releasing a chlorocarbo cation; this latter could add a fluoride anion leading to the *gem*-fluorochloro product **4** (Scheme 3). Similarly, attack by a chloride anion could form the *gem*-dichloro analogue **3**.

The *gem*-difluoride could be the result of a halogen exchange, owing to the exothermicity of the reaction.



Scheme 3.

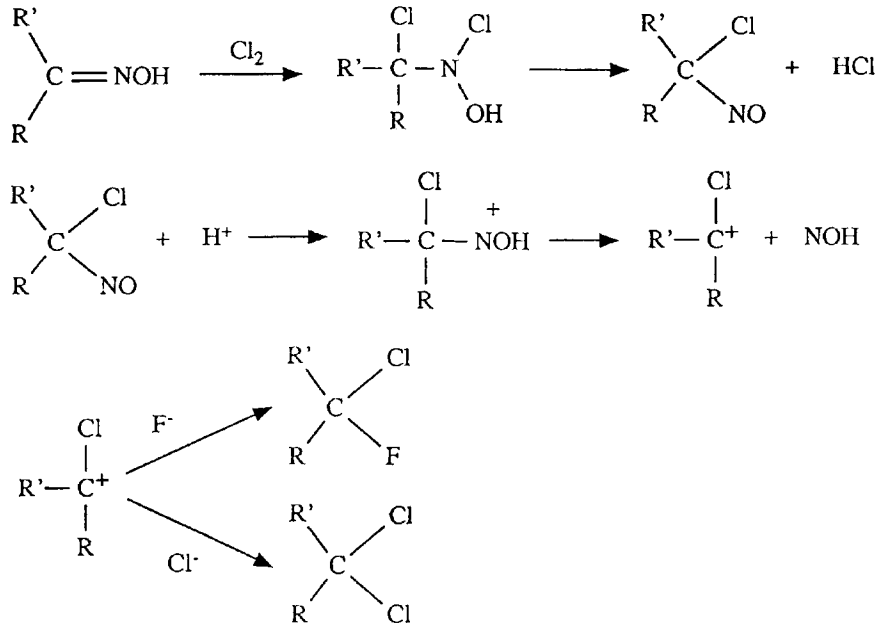
Table 1
Reaction conditions and products formed in the oxidation of oximes in various solvents

No.	Method[a]	Oxime (1)	Oxidant	Solvent	Reaction products		
					Difluoro compound 5 (%)	Fluorochloro compound 4 (%)	Dichloro compound 3 (%)
1	A	**1a**	Cl_2	–	**5a** (20)		
2	A	**1a**	Cl_2	CH_2Cl_2	**5a** (50)		
3	A	**1a**	Cl_2	pentane	**5a** (20)	**4a** (15)	
4	B	**1a**	NOCl	Et_2O		**4a** (45)	[b]
5	B	**1a**	N_2O_4	Et_2O	**5a** (50)		
6	B	**1a**	N_2O_5	Et_2O	**5a** (50)		
7	B	**1a**	Cl_2	Et_2O		**4a** (42)	**3a** (44)
8	B	**1a**	Cl_2	EtOH		**4a** (59)	**3a** (32)
9	A	**1b**	Cl_2	–		**4b** (26)	**3b** (10)
10	B	**1b**	Cl_2	Et_2O		**4b** (13)	**3b** (53)
11	A	**1c**	Cl_2	–	**5c** (21)		
12	B	**1c**	N_2O_4	Et_2O	**5c** (58)		
13	A	**1d**	Cl_2	–	**5d** (33)	**4d** (5)	
14	B	**1d**	Cl_2	Et_2O		**4d** (41)	**3d** (41)
15	A	**1e**	Cl_2	–	**5e** (9)	**4e** (18)	

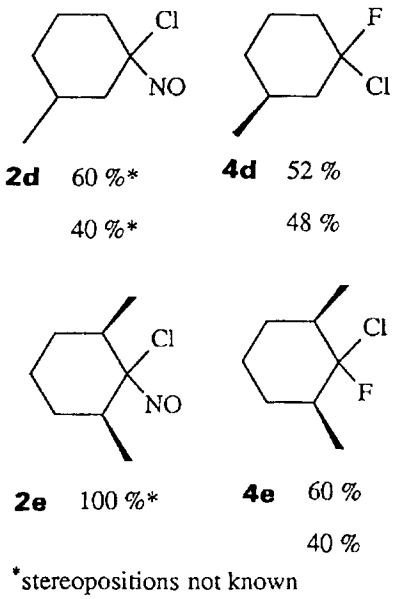
[a]A: Two-step procedure; B: one-step procedure.
[b]1-Chlorocyclohexene was also produced (10%).

We did not think that this exchange would occur at an appreciable rate at 0 °C [5,6] because we did not observe this process during the one-step procedure.

The same experiments, carried out with a 30% aqueous hydrofluoric acid solution, did not give *gem*-dihalogeno compounds. This observation confirms the absence of the transformation when the medium is not sufficiently acidic [31] and explains why this simple formation of *gem*-dihalogenoalkanes has not been described until now. Of course, the acid strength is very



Scheme 4.



Scheme 5.

dependent on the quantity of water present in the medium [38,39]. On the other hand, other oxidants can be used in the hydrogen fluoride medium, provided they do not release nucleophilic species. The use of nitric oxide (entry 6) or dinitrogen tetroxide (entry 5) produced *gem*-difluorocyclohexanes **5a** from **1a** whereas nitrosyl chloride gave a mixture of *gem*-chlorofluorocyclohexane **4a** and 1-chlorocyclohexene (entry 4). This last product evidently results from the loss of a proton from a possible chlorocarbo cation intermediate.

The postulated hyponitrous acid NOH released in the medium (Scheme 4) can be transformed into dinitrogen oxide and water as observed during the hydrolysis of chloronitroso compounds to an oxime and ketone which occurred via electrophilic assistance [37].

$$2NOH \longrightarrow HON{=}NOH \xrightarrow{H^+} H_3O^+ + N_2O$$

4. Experimental details

^1H and ^{13}C NMR spectra were recorded on Bruker AM 300 or AC 200 spectrometers and are expressed in parts per million (δ_H and δ_C) downfield from tetramethylsilane. ^{19}F NMR spectra were obtained on Varian EM360L, AM 200 and AC 200 spectrometers and are recorded in ppm (δ_F) downfield from trichlorofluoromethane (solvent, $CDCl_3$). ^{13}C NMR spectra of the *gem*-chloronitrosoalkanes and -cycloalkanes are reported in Table 2 and of the products in Table 3. Anhydrous hydrogen fluoride was purchased from Setic Labo while organic reactants were obtained from Aldrich. Non-commercial oximes were prepared according to reported procedures [40]. **CAUTION: anhydrous hydrogen fluoride is reactive and corrosive [36].**

4.1. Two-step procedure

Preparation of gem-chloronitrosoalkanes 2

gem-Chloronitrosoalkanes **2** were prepared according to the method of Müller et al. [41]. Chlorine was bubbled into a mixture of diethyl ether and oxime at 0 °C. The appearance of a deep blue colour was characteristic of chloronitrosoalkane formation. The organic phase was washed with 10% sodium carbonate solution and brine, and then dried over magnesium

Table 2
^{13}C NMR spectra of *gem*-chloronitrosoalkanes and -cycloalkanes

Compound	Spectral shift (δ, ppm)								
	C1	C2	C3	C4	C5	C6	C7	C8	C9
2a	122.5	33.1	21.6	24.4					
2d (60%)	119	40.2	32.2	27.9	21.7	33.3	21.2		
(40%)	109.1	44.6	33	30	23.3	36.1	22.1		
2e	126.7	45.6	33.8	26.3			14.7		
2b	122.7	38.1	25.5						
2c	23.3	117	38.4	24	29.2	28.7	31.5	22.4	14

Table 3
^{13}C NMR spectra of the products[a]

Compound	Spectral shift (δ, ppm)						
	C1	C2	C3	C4	C5	C6	C7 C8 C9
5a	123 (t) 241	33.8 (t) 23.6	22.5 (t) 5	24.8			
5a (lit. value [43])	123.7 241	34.6 23.5	23.5 5	24.9			
4a	115 (d) 245	40.4 (d) 21	23.2 (d) 4.5	24			
3a	91.7	46.2	23.7	24			
4b	118.6 (d) 250	42 (d) 22	22.5 (d) 1.5				
3b	91.6	47.7	22.7				
5c	22.6 (t) 28	123.6 (t) 237	37.6 (t) 25	23.4	29.3 28.9		31.3 22 13
5d	124 (dd) 247 246	42.2 (dd) 26 25	29.8 (d) 8	33.1 (t) 4	22.1 (d) 9	33.8 (t) 25.4	22.2
4d (F eq.)	116 (d) 247	48.2 (d) 18	30	32.7	21.4	39.8 (d) 19	22.9
4d (F ax.)	114 (d) 247	49 (d) 23	29.8	33.3	21.6	40.3 (d) 23	23
3d	91.4	54.3	30	33	21.4	45.9	23.6
5e	–	38.8 (t) 24	31.5 (t) 5	25.4			14.4 (t) 5
4e (F ax.)	– –	44.4 (d) 22	31.7 (d) 5	24.6			15.4 (d) 6
4e (F eq.)	123 (d) 248	43.4 (d) 19	31.5 (d) 5	24.7			14.5 (d) 4
6	29.7 (d) 4	113.6 (d) 242	40.3 (d) 23	29.6 (d) 4	58 (d) 21	85 (d) 176	
7	27.5 (d) 21	133.7 (d) 243	39.3 (d) 23	31.1 (d) 24	91 (d) 176	45.3 (d) 25	
8	37.3	90	47.7 (d) 4	28.7 (d) 21	91.3 (d) 176	45.3 (d) 25	

[a]Fluorine–carbon coupling constants (in Hz) are reported in the second row for each compound.

sulfate. After evaporation of the solvent, the product obtained was stored away from light. Its purity was determined by ^{13}C NMR spectroscopy (Table 2).

Fluorination of chloronitroso compounds

Pure anhydrous hydrogen fluoride (10 ml), optionally diluted with a cosolvent (10 ml), was stirred at −10 °C in a polypropylene flask. The deep blue coloured chloronitrosoalkane **2** (5 g), optionally dissolved in a solvent (3 ml), was poured slowly into the medium. The mixture immediately became brown. After stirring for 2 h the mixture was poured on to ice (100 g) and extracted with pentane. The organic layer was washed with concentrated sodium hydrogen carbonate solution and brine, then dried over magnesium sulfate. After removal of the solvent with a spinning-band distillation apparatus, the residue was analysed and separated by GLC (column 30% SE 30, 150 °C).

1-Chloro-1-nitrosocyclohexane (**2a**): In pure anhydrous hydrogen fluoride, the following products were obtained: difluorocyclohexane (**5a**) (yield, 20%) (δ_F: −95.9 (m) ppm [lit. value [42]: −96 ppm]; MS *m/e*: 120; 119; 101; 100; 81), cyclohexanone (30%), dichloro-1,1-cyclohexane (**3a**) (a few per cent) and phenol (traces); with dichloromethane as cosolvent, difluorocyclohexane (**5a**) (50%) was produced. Difluorocyclohexane (**5a**) (20%) and chlorofluorocyclohexane [5] (**4a**) (15%) (δ_F: −93 ppm; MS *m/e*: 101; 100; 81) were formed in the HF/pentane mixture. In the pure HF experiment, the extraction of the aqueous phase after neutralisation gave cyclohexanone-oxime (**1a**) in 30% yield.

1-Chloro-1-nitrosocyclopentane (**2b**): In pure anhydrous hydrogen fluoride, the following products were obtained: chlorofluorocyclopentane (**4b**) (26%) (δ_F: −95.6 (quintuplet) ppm, J_{HF} = 19.3 Hz; MS *m/e*: 103; 105; 86; 67), dichlorocyclopentane (**3b**) (10%) (δ_H: 2.13; 1.9 ppm; MS *m/e*: 103; 105; 67) and cyclopentanone-oxime (8% isolated after basic extraction).

2-Chloro-2-nitrosononane (**2c**): In pure anhydrous hydrogen fluoride, the following products were obtained: 2,2-difluorononane (**5c**) (21%) (δ_F: −90 (sextuplet) ppm, J_{HF} = 17 Hz), nonan-2-one (32%) and nonan-2-one-oxime (37% isolated after basic extraction).

1-Chloro-1-nitroso-3-methylcyclohexane (**2d**): In pure anhydrous hydrogen fluoride, the following products were obtained: 1,1-difluoro-3-methylcyclohexane (**5d**) (33%) (δ_F: −96; −98 ppm, J_{FF} = 235 Hz; MS *m/e*: 115; 99; 95; 85; 67; 59; 45), 1-chloro-1-fluoro-3-methylcyclohexane (**4d**) (5%) (52:48 mixture of F equatorial/axial non-separated isomers) (δ_F (equatorial): −85.8 ppm; δ_F (axial): −106 (m) ppm; MS *m/e*: 131; 95; 79; 67; 55) and 3-methylcyclohexanone (36%).

1-Chloro-1-nitroso-2,6-*cis*-dimethylcyclohexane (**2e**): In pure anhydrous hydrogen fluoride, the following products were obtained: 1,1-difluoro-2,6-*cis*-dimethylcyclohexane (**5e**) (9%) (δ_F(equatorial): −102 (large d) ppm, J_{FF} = 235 Hz; δ_F(axial): −129 (large dt) ppm. J_{FF} = 235 Hz, J_{HF} = 27 Hz; MS *m/e*: 148; 128; 113; 109; 97; 86; 77; 69; 55); 1-chloro-1-fluoro-2,6-*cis*-dimethylcyclohexane (**4e**) (18%) (60:40 mixture of F equatorial/axial non-separated isomers) (δ_F(equatorial): −99.2 (large s) ppm; δ_F(axial): −132.6 (large t) ppm, J_{HF} = 28 Hz; MS *m/e*: 128; 113; 109; 99; 94; 86; 81; 73; 67; 59; 55) and 2,6-*cis*-dimethylcyclohexanone (10%).

4.2. One-step procedure

Using chlorine

Anhydrous hydrogen fluoride (10 ml) was condensed at −10 °C into a polypropylene flask containing the oxime (5 g) and diethyl ether (or ethanol) (50 ml). Then chlorine was bubbled into the mixture. The reaction began a few minutes later. Chlorination was stopped when the deep blue characteristic colour of the nitroso derivatives had vanished and the mixture became brown. After 4 h stirring, the colour was red. The mixture was hydrolysed with ice (100 g) and extracted with pentane. The organic layer was washed with 10% sodium carbonate and brine, then dried over magnesium sulfate. After removal of the solvent, the products (as listed below for various starting materials) were analysed and separated by GLC.

Cyclohexanone-oxime (**1a**): Chlorofluorocyclohexane (**4a**) (42%) and dichlorocyclohexane (**3a**) (44%) (identical to the compound prepared by the usual reaction of cyclohexanone with phosphorus pentachloride) were obtained using diethyl ether as cosolvent. Their yields were 59% and 32%, respectively, when the ether was replaced by ethanol. In this latter case, important amounts of chloroacetaldehyde diethylacetal (^{13}C NMR δ: 101.4; 62.1; 43.6; 13.9 ppm) were also produced.

Cyclopentanone-oxime (**1b**): Chlorofluorocyclopentane (**4b**) (13%) and dichlorocyclopentane (**3b**) (53%) were obtained using diethyl ether as cosolvent.

3-Methylcyclohexanone-oxime (**3d**): In pure anhydrous hydrogen fluoride, the following products were obtained: non-separated isomers of **4d**: *r*-1-Chloro-1-fluoro-*t*-3-methylcyclohexane (16%) and *r*-1-chloro-1-fluoro-*c*-3-methylcyclohexane (25%); 1,1-dichloro-3-methylcyclohexane (**3d**) (41%).

Hex-5-en-2-one-oxime (**1e**): Products formed in hydrogen fluoride using diethyl ether as cosolvent were separated by GLC (SE30 column) between 150 °C and 220 °C. The ratios were 0.34, 0.22 and 0.44 for 1,5-dichloro-2,5-difluorohexane (**6**) (δ_F: −95 (m); −183 (m) ppm), 2-chloro-2,6-difluorohexane (**7**) (δ_F: −94 (m); −216 (tt) ppm), and 1,5,5-trichloro-2-fluorohexane (**8**) (δ_F: −183 (m) ppm).

Using other oxidants

A mixture of **1a** (3 g), diethyl ether (50 ml) and anhydrous hydrogen fluoride (10 ml) was stirred at

−10 °C in a propylene flask. The gas from a second flask containing 99% nitric acid was carried along by an argon flow into the propylene flask. At the end of the reaction the blue coloured mixture became yellow. This mixture was stirred for 1 h more. After hydrolysis with ice (100 g), extraction with pentane, washing with 10% sodium carbonate and brine, drying over magnesium sulfate, the organic layer was distilled with a spinning-band column. The *gem*-difluorocyclohexane **5a** was obtained in 50% yield. The result was identical when commercial dinitrogen tetroxide was used as oxidant. The experiment was repeated with nitrosyl chloride at −10 °C. There was a strong release of gas. At the end of the reaction, the blue mixture became colourless. After usual treatment, chlorofluorocyclohexane (**4a**) (45%) and 1-chlorocyclohexene (11%) (identical to the compound prepared by the usual reaction of cyclohexanone with phosphorus pentachloride) were obtained.

The dinitrogen tetroxide experiment was repeated with nonan-2-one-oxime (**1c**) (3 g) when 2,2-difluorononane (**5c**) was obtained in 58% yield (δ_F: −90.2 (sextuplet) ppm, J_{HF} = 17 Hz).

5. Conclusions

The oxidation of oximes in strong acids allows the preparation of *gem*-difluoro, -chlorofluoro and -dichloro alkanes or cycloalkanes. In the majority of these experiments, mixtures of *gem*- dihalogenoalkanes were obtained, but they may be transformed into single *gem*-difluoro derivatives by halogen exchange. This method, which avoids the use of fluorine or sulfur tetrafluoride, can be performed with cheap and readily available reagents (chlorine, hydrogen fluoride).

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