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PREPARATION OF TWO 1-PHENYL-CHLOROFLUOROPROPENES

Wojciech DMOWSKI

Institute of Organic Chemistry, Polish Academy of Sciences,
00-961 Warsaw (Poland)

SUMMARY

1-Phenyl-2-chloro-3,3,3-trifluoropropene and 1-phenyl-1,2-dichloro-3,3,3-trifluoropropene were prepared from 1-phenyl-3,3,3-trifluoropropene by a chlorination-dehydrochlorination sequence. Intermediate 1-phenyl-1,2-dichloro-3,3,3-trifluoropropane and 1-phenyl-1,2,2-trichloro-3,3,3-trifluoropropane were also isolated. All compounds were characterised by elemental analysis, boiling points, ^{1}H and ^{19}F NMR spectra.

INTRODUCTION

In connection with planned kinetic investigations on nucleophilic substitution of vinylic halogen atoms in 1-phenyl-polyhalogenopropenes, an appropriate amount of 1-phenyl-1,2-dichloro-3,3,3-trifluoropropene was required. 1-Phenyl-3,3,3-trifluoropropene $\underline{1}$, easily obtained by the lithium aluminium hydride reduction of 1-phenylpentafluoropropene [1], was used as a substrate for synthesis of the required compound. The synthesis involved a four-step chlorination-dehydrochlorination process which,

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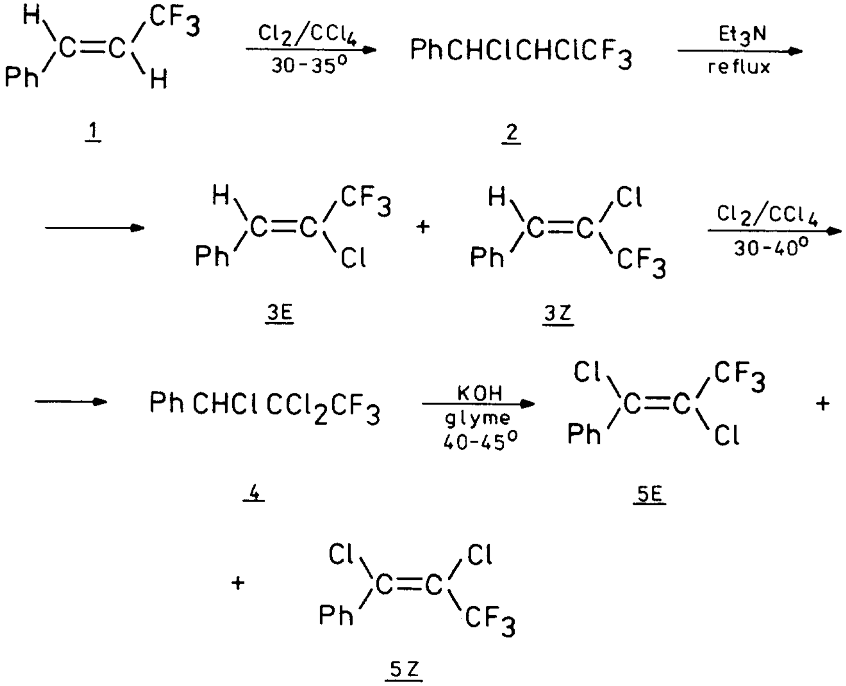
in general, followed the bromination-dehydrobromination procedure described by Yagupolskii and Fiyalkov [2].

RESULTS AND DISCUSSION

The reaction sequence is shown on the scheme below:

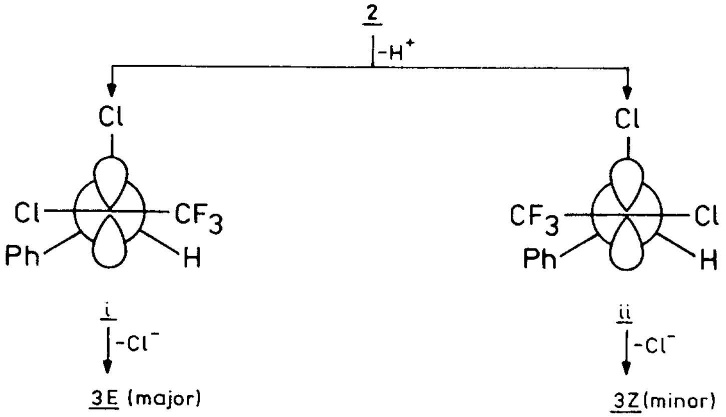


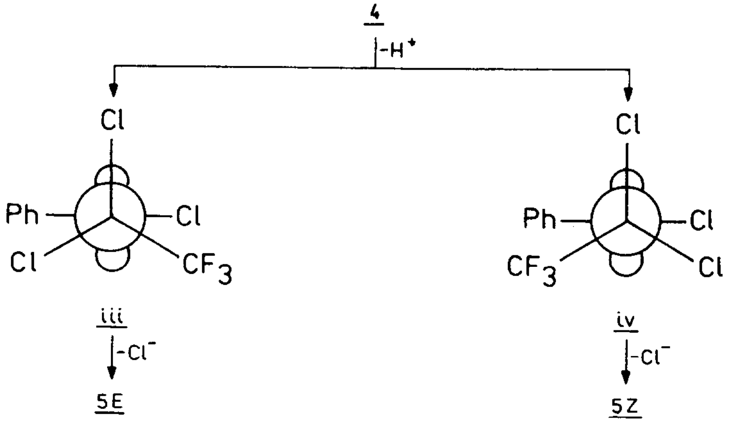
Chlorination of 1-phenyl-3,3,3-trifluoropropene 1 proceeded readily without irradiation or heating. A moderate exothermic effect occurred so that the reaction temperature was easily controlled by the rate at which chlorine was introduced. Addition of chlorine across the double bond of alkene 1 to give dichloroalkane 2 was the main course of the reaction with only a little formation of trichloroalkane 4 (*ca*. 3%). In contrast, chlorination of a mixture of 1-phenyl-2-chloro-3,3,3-trifluoropropenes 3E and 3Z to alkane 4 required illumination with a visible light lamp. Formation of a tetrachloro derivative was not observed; a compound (max. 2%) having a longer GLC retention time than trichloroalkane 4 disappeared after treatment with triethylamine which suggested the structure $PhCCl_2CHClCF_3$ for this compound.

1-Phenyl-1,2-dichloro-3,3,3-trifluoropropane 2 refluxed with an excess of triethylamine gave chloroalkenes 3 as the only dehydrochlorination products. No products of the abstraction of benzylic hydrogen were formed; this is in agreement with the expected difference of the acidities of hydrogen atoms α to the CF_3 and to the phenyl group. Attempted dehydrochlorination with triethylamine of compound 4 failed, but when a more basic medium, i.e. a suspension of potassium hydroxide in ethylene glycol dimethyl ether (glyme) was used, exothermic reaction occurred to give alkenes 5 in high yield.

Alkene 1 used in this work consisted of 97 - 98% of the E form and 2 - 3% of the Z form [1]. Chlorination of this alkene proceeded non-stereospecifically to give diastereoisomers of dichloroalkane 2 in a ratio which varied from 1 : 1.5 to 1 : 3.5. Also, dehydrochlorination of 2, and 4 occurred non-stereospecifically. In the case of compound 2, high stereoselectivity for the E form of alkene 3 was observed (E/Z ratio = 4 to 6) while dehydrochlorination of 4 always resulted in formation of equal amounts of alkenes 5E and 5Z. Stereochemical results of the dehydrochlorination reactions can be understood on the basis of conformational stability of the carbanionic intermediates i - iv involved in these reactions.

It has been recently shown [3] that steric requirements of a CF_3 group are greater than those for a chlorine atom, and if so, it is reasonable that conformation i, which by *trans*-elimination of chloride gives alkene 3E should be energetically preferable to conformation ii leading to alkene 3Z. Formation of equimolar amounts of 5E and 5Z from 4 suggests energetic equivalence of conformations iii and iv.





Compounds 2 - 5 were isolated by distillation and their structure was determined from elemental analysis (Table 1) and ^{1}H and ^{19}F NMR spectrometry (Table 2). The NMR spectra of dichloroalkane 2 exhibited double signals both for the CF_3 group and aliphatic protons, thus indicating the presence of two diastereoisomers. Both the CF_3 group and vinylic proton signals in the NMR spectra of the dehydrochlorination products of alkane 2 appeared as singlets which excluded structures other than 3E and 3Z. Assignment of the E and Z isomers of alkenes 3 and 5 was based on a comparison of chemical shifts of the CF_3 group signals of these compounds with the corresponding signals of the E and Z isomers of 1-phenyl-2,3,3,3-tetrafluoropropene and a series of 1-phenylpentafluoropropenes reported earlier [1, 4]. In all 1-phenylfluoroalkenes investigated, so far signals due to CF_3 groups of the E forms appeared at higher field than those for the Z forms.

EXPERIMENTAL

Boiling points were determined by distillation and are uncorrected (Table 1). ^{1}H and ^{19}F NMR spectra (Table 2) were recorded with a Jeol JNM-4H-100 spectrometer and IR spectra with a Beckmann IR Acculab TM-1 spectrometer. The ratios of isomeric compounds and the purity were determined chromatographically with a Chromatron GCHF.18.3.4 instrument (GDR) using a 3.5 x 4 mm column packed with Chromosorb G coated with 3% silicon oil SE-52.

Triethylamine was purified by storage over sodium hydroxide pellets and distillation. Ethylene glycol dimethyl ether (glyme) was refluxed with sodium metal until blue with benzophenone and was then distilled. Synthesis of 1-phenyl-3,3,3-trifluoropropene 1 has been described in the preceding paper [1].

TABLE 1

Physical properties and analysis of compounds 2 - 5

Compound	Purity	B.p.	Found (Calculated)			
	(GLC %)	°C(Torr)	C	H	F	Cl
2 A/B=1.5	96.0	88 - 94(15)[a]	44.5(44.5)	2.9(2.9)	23.3(23.5)	29.1(29.2)
3 E/Z=4.3	99.2	78 - 80(16)	52.2(52.3)	2.8(2.9)	27.7(27.6)	17.2(17.2)
4	95.2	96 - 98(2)	38.9(39.0)	2.0(2.2)	20.6(20.5)	38.2(38.3)
5 E/Z=1	99.0	92 - 98(35)	44.6(44.9)	1.9(2.1)	23.7(23.7)	29.4(29.4)

IR : v(C=C) = 1642 and 1650 cm^{-1} for 3, 1602 and 1618 cm^{-1} for 5.

[a] In agreement with the reported value [2].

TABLE 2

^{1}H and ^{19}F NMR data of compounds 2 - 5

Compd.	Chemical shifts (ppm)^a				
	$\phi(CF_3)$	$\delta(H^1)$	$\delta(H^2)$	$\delta(Ph)$	
2	69.8(d)	5.20(d)	4.40(qd)	7.37(5H)	$^3J(HF)$= 6.3 Hz $^3J(HH)$=6.5 and 4.3Hz
	70.8(d)	5.30(d)	4.60(qn)		
3Z	61.8(s)	7.20(s)^b		7.33(3H),7.65(2H)	
3E	69.0(s)				
4	73.5(s)	5.70(s)		7.25(3H),7.45(2H)	
5Z	59.4(s)			7.25(3H),7.30(2H)	
5E	61.4(s)				

s - singlet, d - doublet, q - quartet, qn - quintet

[a] From internal CCl_3F for ^{19}F spectra (positive upfield) and from internal TMS for ^{1}H spectra.

[b] Overlapping with the aromatic protons signals.

All distillations were performed using a 10 cm long adiabatic Vigreux-type column and a distillation head.

Chlorination of 1-phenyl-3,3,3-trifluoropropene 1

To a solution of 24 g (0.14 mole) of alkene 1 (E/Z = ca. 40) in 50 ml of carbon tetrachloride contained in a 250 ml glass reactor equipped with thermometer, magnetic stirring bar, inlet tube for chlorine and outlet tube connected to two washers (the first empty, the second filled with aqueous solution of sodium hydroxide), gaseous chlorine was introduced at such a rate as to be fully absorbed and to keep the reaction temperature within the range of 30 - 35°. After six hours, the reaction mixture was shown by GLC to contain, besides carbon tetrachloride, 93.4% of dichloroalkane 2 (two diastereoisomers), 1.2% of unreacted alkene 1, 0.9% of alkene 3, and 3.2% of alkane 4 (minor components were identified by a comparison of their retention times with those of authentic samples).

The excess of chlorine was removed with a stream of nitrogen introduced beneath the surface of the solution and then the solvent was distilled off under atmospheric pressure. The residue was vacuum-distilled to give 28.8 g of 1-phenyl-1,2-dichloro-3,3,3-trifluoropropane 2 of a 96% purity. Yield, 85 mol %.

Dehydrochlorination of 1-phenyl-1,2-dichloro-3,3,3-trifluoropropane 2

27.2 g (0.112 mole) of alkane 2 and 110 ml of freshly distilled triethylamine were refluxed for ten hours. A precipitate of the amine hydrochloride was formed. The reaction mixture was acidified, while cooling, with diluted (1 : 1) hydrochloric acid, the organic layer was extracted with ether and the extract was dried over magnesium sulphate. Vacuum-distillation gave 18.5 g of a fraction containing 94.5% of alkenes 3, 2,4% of alkane 2, and 3.1% of alkane 4. Yield, 80 mol %. Redistillation gave 1-phenyl-2-chloro-3,3,3-trifluoropropene 3 (E/Z = 4.3) of a 99% purity.

Chlorination of 1-phenyl-2-chloro-3,3,3-trifluoropropene 3

A solution of 17.9 g (0.09 mole) of alkene 3 in 30 ml of carbon tetrachloride was chlorinated as described above using external illumination with a 100 W visible-light lamp. The lamp was placed at such a distance from the reactor as to keep the reaction temperature within the range of 30 - 40°. The reaction was completed in five hours. GLC of the crude reaction mixture: 94.0% of 4, 3.4% of 2, 0.9% of 5, and 1.7% of $PhCCl_2CHClCF_3$ (probable structure). Distillation gave 23.6 g of 1-phenyl-1,2,2-trichloro-3,3,3-trifluoropropane 4 of a 95.2% purity. Yield, 98 mol %.

Dehydrochlorination of 1-phenyl-1,2,2-trichloro-3,3,3-trifluoropropane 4

17.0 g (0.06 mole) of alkane 4 was added dropwise to a stirred suspension of 20.0 g (0.36 mole) of powdered potassium hydroxide in 60 ml of ethylene glycol dimethyl ether. An exothermic reaction occurred and the temperature increased to 40°. Stirring was continued for four hours using slight external heating to keep the reaction temperature within the range of 35 - 40°. Dilute hydrochloric acid (1 : 1) was added in such amount as to dissolve the precipitate of potassium chloride, then the organic layer was extracted with chloroform and the extract was washed with water until neutral and dried over calcium chloride. Distillation gave 10 g of 1-phenyl-1,2-dichloro-3,3,3-trifluoropropene 5 (E/Z = 1) of a 99% purity. Yield, 68 mol %.

ACKNOWLEDGMENT

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Note: In the next series of reactions aimed at preparing larger quantities of alkenes 3 and then 5, crude alkanes 2 and 4, after removal of the solvent, were dehydrochlorinated. This resulted in slightly improved yields of the alkenes.