Journal of Fluorine Chemistry, 18 (1981) 25–30

Received: October 31, 1980

An Improved Synthesis of 1-Phenylpentafluoropropenes

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SUMMARY

1-Phenylpentafluoropropene and a number of its para- and ortho-substituted derivatives were prepared in high yields by reaction of hexafluoropropene with etheral solutions of corresponding phenylmagnesium bromides in sealed glass tubes under autogenous pressure. The products were obtained as mixtures of the Z and E isomers, which ratios varied from 1/2 to 1/6 in favour of the E forms. ^{19}F n.m.r. and i.r. spectra and b.p. of the 1-phenylpentafluoropropenes are reported.

INTRODUCTION

The classical route to fluoroolefins of the type RCF=CFX, where X is F, Cl or R_f and R is alkyl or aryl, involves reactions of fluoroolefins CF_2=CFX with organolithium compounds RLi [1] . Reactions of phenyllithium with a number of perhaloolefins were carried out to give 1-phenyl substituted olefins in 20 - 60 % yields together with products formed by succesive replacement of vinylic fluorines by phenyl groups. 40 - 50 % yields of 1-phenylpentafluoropropene and some of its ring substituted analogs (p- and m-fluoro) were obtained by reactions of hexafluoropropene with the corresponding Grignard reagents [2,3] . The reaction of hexafluoropropene with p-$CF_3C_6H_4$MgBr gave only a 11 % yield of 1-(p-trifluoromethyl)phenylpentafluoropropene [4] .

For some of our research we required moderate quantities of 1-phenylpentafluoropropene and its para- and ortho-substituted derivatives. We therefore sought an improved method of their synthesis involving Grignard reagents. According to the procedure previously described [1,2] , gaseous fluoroolefin is passed into a solution of organometallic compound under atmospheric pressure at a rate at which it is consumed. Under these conditions the concentration of the reactant olefin in the reaction medium is low and the yield of the required mono-substituted product is low; this is due to further reaction of the olefin with an excess of organometallic compound to give di- and polysubstituted olefins.

RESULTS

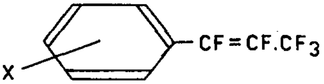
It has been found that yields of 1-phenyl substituted pentafluoropropenes can be effectively improved by reaction of hexafluoropropene with etheral solutions of phenylmagnesium bromides in sealed glass tube under autogenous pressure. Thus, 1-phenylpentafluoropropene and a number of its para- and ortho-substituted derivatives were prepared in high yields. The ortho- and para-derivatives are reported for the first time. The results are summarised in Table 1, As expected, 1-(p-trifluoromethyl)phenylpentafluoropropene was obtained in relatively poor yield, but more than three times higher than previously reported yield [4] . Similarly a poor yield of 1-(o-chloro)phenylpentafluoropropene was obtained.

Attempted reactions of phenylmagnesium bromide with $CF_2=CF_2$, $CF_2=CFCl$, and $CF_3CF=CFCF_3$ failed; only trace amounts of phenyl substituted olefins were formed. Isolation of large quantities of benzene after hydrolysis of the reaction mixtures indicates that the above olefins are not sufficiently electrophilic to react with an aryl Grignard reagent. Nitroderivatives of 1-phenylpentafluoropropene also cannot be obtained by this method because of the low reactivity of nitrophenylmagnesium bromides.

The 1-phenylpentafluoropropenes were formed as mixtures of geometric isomers. Comparison of integrated ^{19}F n.m.r. spectra with g.l.chromatograms allowed us to identify shorter and longer retention isomers as the Z and E forms, respective-

TABLE 1

Physical properties and yields of 1-phenylpentafluoropropenes



Compound X	Boiling range (°C)	$\nu_{C=C}$ (cm^{-1})	Z/E ratio[a]	Isolated yield (mole %)	Purity[b] (%)
H	149-151[c]	1725(Z) 1710(E)	17/83	70.1[d]	99.0
p-CH_3	176-177	1715(Z) 1707(E)	20/80	72.2	99.0
o-CH_3	158-160	1720	20/80	91.0	94.3
p-CH_3O	205-206	1715(Z) 1705(E)	20/80	72.5	90.0
o-CH_3O	191-192	1720	36/64	78.5	96.8
p-Cl	172-173	1720(Z) 1708(E)	18/82	75.6	93.8
o-Cl	134-136	1700	12/88	32.0	96.0
p-CF_3	160-161[e]	1710(Z) 1700(E)	14/86	36.0[f]	97.5

a) G.l.c. estimates

b) G.l.c. estimates. Impurities are C_6H_5X and BrC_6H_4X .

c) Lit: 149° for E and 139° for Z [4] .

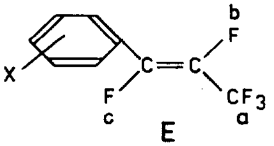
d) Reported yield 42 % [2] .

e) Lit: 163° for E and 159° for Z [4] .

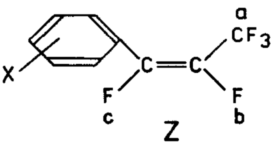
f) Reported yield 11 % [4] .

TABLE 2

^{19}F n.m.r. data of 1-phenylpentafluoropropenes [a]



E



Z

Compound		Chemical shift (p.p.m.)[b]			Coupling constant(Hz)		
X		$\phi(F_a)$	$\phi(F_b)$	$\phi(F_c)$	$J(F_aF_b)$	$J(F_aF_c)$	$J(F_bF_c)$
H	E	69.9(dd)	170.0(dq)	146.8(dq)	10.5	22.3	131.0
	Z	66.0(dd)	154.8(qd)	110.0(qn)	13.2	8.0	8.0
p-CH_3	E	67.1(dd)	170.8(dq)	146.9(dq)	10.5	22.3	131.0
	Z	65.7(dd)	155.3(qd)	109.4(dq)	13.0	8.1	9.4
o-CH_3	E	67.7(dd)	168.2(dq)	128.0(dq)	10.7	21.6	141.0
	Z	66.8(dd)	154.7(qn)	105.5(m)	12.6	7.8	12.6
p-CH_3O	E	69.9(dd)	172.6(dq)	146.4(dq)	10.8	22.3	130.6
	Z	65.8(dd)	155.0(qd)	108.0(dq)	13.2	8.2	10.8
o-CH_3O	E	67.7(dd)	167.8(dq)	131.5(dq)	11.5	22.1	141.4
	Z	67.7(dd)	155.7(qn)	108.8(dq)	12.5	8.0	12.5
p-Cl	E	67.5(dd)	168.6(dq)	147.4(dq)	10.1	22.0	131.0
	Z	66.0(dd)	153.4(qd)	110.3(qn)	12.6	8.0	8.0
o-Cl	E	66.2(dd)	168.4(dq)	145.0(dq)	11.0	22.3	132.5
	Z	65.6(dd)	153.3(qd)	108.8(dq)	13.5	8.0	9.5
p-CF_3[c]	E	67.7(dd)	166.8(dq)	148.5(dq)	9.9	22.0	131.0
	Z	66.2(dd)	153.0(qd)	112.2(qd)	12.0	7.6	5.7

d - doublet, q - quartet, qn - quintet, m - multiplet

a) ^{1}H n.m.r. spectra of all compounds exhibit signals of the aromatic ring and, if present, signals of CH_3 group.

b) Positive upfield from CCl_3F .

c) $\phi(p\text{-}CF_3)$ = 64.0(s) for the E form, and 62.0(s) for the Z form.

ly. The isomer ratios varied from 1/2 to 1/6 in favour of isomer E. This stereoselectivity is consistent with the expected differences of the steric strains in the reactive intermediates, which by trans-elimination of MgBrF yield one or the other isomer.

^{19}F n.m.r. parameters of the Z and E isomers of 1-phenylpentafluoropropenes (Table 2) are in agreement with the data reported for $C_6H_5CF{=}CFCF_3$ [4,5] ,p-$CF_3C_6H_4CF{=}CFCF_3$ [4] , and p-F-$C_6H_4CF{=}CFCF_3$ [3] .

EXPERIMENTAL

All compounds were investigated as mixtures of the E and Z isomers. Boiling points(uncorrected) were determined in a capillary by the Sivilobov method. ^{19}F n.m.r. spectra were recorded with a JEOL JNM-4H-100 spectrometer. Chemical shifts (positive upfield) are in p.p.m. from internal CCl_3F. I.R.spectra were recorded with a Beckmann IR 4240 spectrometer. G.l.c. analyses were performed with a Chromatron GCHF.18.3.4 instrument (G.D.R.) using a 3.5 m x 0.4 cm column filled with Chromosorb G coated with 3 % silicon oil SE-52.

General procedure

Etheral solutions of phenylmagnesium bromides (0.2-0.6 mole) were placed in a pressure glass tube of 300ml or 500ml capacity equipped with a Rotaflo valve. The reactor was then cooled in liquid nitrogen, evacuated and an equimolar amount of hexafluoropropene was then condensed into the tube. After closing the tube was warmed slowly to ambient temperature and shaken mechanicaly for 20 hours (40 hours in the case of $CF_3C_6H_4MgBr$). Upon completion of the reaction, the pressure was reduced by opening of the valve (usually little or no pressure remained) and the reaction mixture was hydrolysed with hydrochloric acid and extracted with ether. The extracts were dried with $MgSO_4$ and after removal of the solvent the residue was distilled through a short column under reduced pressure.

Caution: an attempt to carry out the reaction of phenylmagnesium bromide with hexafluoropropene on a 0.8 mole scale resulted in an explosion. Other reactions on this scale were not attempted.

ACKNOWLEDGMENT

The author thanks Mr.B.Lutosławski for carrying out the syntheses.

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