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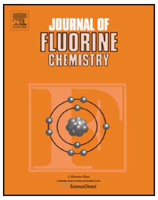

Generation of perfluorinated 1-alkylbenzocyclobuten-1-yl and 1-alkylindan-1-yl cations. On paradoxical stabilizing influence of an electron-withdrawing perfluoroisopropyl group on the relative stabilities of the cations

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ABSTRACT

When perfluoro-1-alkylbenzocyclobutenes and -indanes were dissolved in an excess of SbF_5, perfluorinated alkylbenzocycloalken-1-yl cations containing a fluorine atom or a perfluoroalkyl group in the cationic centre were generated. Contrary to expectations, a number of stable long-lived perfluoro-1-isopropylbenzocycloalken-1-yl cations containing an electron-withdrawing perfluoroisopropyl group in the cationic centre have been obtained. The DFT (B3LYP/6-31G*) calculations showed that the relative stabilities of isomeric cations containing a fluorine atom or a perfluoroalkyl group in the cationic centre change in favor of cations containing a perfluoroalkyl group in the cationic center when going from a CF_3 to a $CF(CF_3)_2$ group.This is in accordance with the experimental data.

1. Introduction

A number of electrophilic reactions of polyfluoroorganics proceed via fluorinated carbocationic species as intermediates [1–6]. Moreover, relatively stable long-lived fluorocarbocations, including perfluorinated carbocations have been generated [1–16]. It should be noted that a fluorine atom directly attached to the cationic centre or located in a resonance position of a cation has a stabilizing influence on the cation [17–20]. In contrast, a carbocation is destabilized by introducing an electron-withdrawing perfluoroalkyl group in the cationic centre or in a resonance position of the carbocation [8–10,21–23]. Electronic effects of perfluorinated alkyl groups CF_3, C_2F_5, $CF(CF_3)_2$ are close to each other [22,23], their σ_p (σ_I, σ_R) and σ_m values calculated from ^{19}F n.m.r. chemical shifts of substituted fluorobenzenes are equal to 0.49 (0.39, 0.10), 0.52 (0.41, 0.11), 0.52 (0.48. 0,04) and 0.44, 0.47, 0.50 [22,23], respectively and their van der Waals volumes are significantly different [2,24].

A competition between electronic and steric factors in the corresponding intermediate benzylic carbocations (Fig. 1) resulted, for example, in different orientations in SbF_5-catalysed reactions of perfluorinated 1-alkylbenzocycloalkenes with fluoroolefins [25,26].

Thus, perfluoro-1-ethylindane reacts with tetrafluoroethylene via intermediate cation of ‘b’-type to give only perfluoro-1,1-diethylindane. In contrast, analogous reaction of perfluoro-1-ethyltetralin proceeds via cation of ‘a’-type to form perfluoro-1,4-diethyltetralin [25]. In the case of perfluorinated 1-methyl- and 1-ethylbenzocyclobutenes the both cations give corresponding alkylation products in almost equal amounts [25,26]. It was interesting to generate cations from a series of perfluorinated 1-alkylbenzocycloalkenes with different perfluoroalkyl groups in order to study the effect of the perfluoroalkyl group on the relative stabilities of the isomeric cations of ‘a’- and ‘b’-types. This work describes the generation of perfluorinated alkylbenzocyclobutenyl and alkylindanyl cations with CF_3, C_2F_5, $CF(CF_3)_2$ groups including unexpectedly stable perfluoro-1-isopropylbenzocyclobuten-1-yl and perfluoro-1-isopropylindan-1-yl cations.

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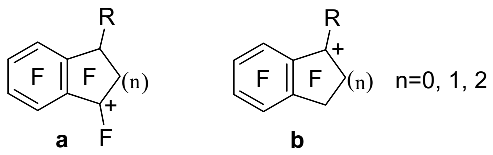


Fig. 1. Isomeric benzylic carbocations from perfluorobenzocycloalkenes.

2. Results and discussion

2.1. Generation of cations

When perfluoro-1-alkylbenzocyclobutenes were dissolved in an excess of SbF_5 (~20 mol per mole of the substrate) with addition of SO_2ClF, perfluorinated 2-alkylbenzocyclobuten-1-yl and 1-alkylbenzocyclobuten-1-yl cations were generated. Thus, perfluoro-1-methylbenzocyclobutene (**1**) gave perfluoro-2-methylbenzocyclobuten-1-yl cation (**1a**) with the equilibrium between cation **1a** and precursor **1** being shifted towards the precursor (Scheme 1). Similarly, perfluoro-2-ethylbenzocyclobuten-1-yl (**2a**) and perfluoro-1-ethylbenzocyclobuten-1-yl (**2b**) cations were generated from perfluoro-1-ethylbenzocyclobutene (**2**), but in this case cation **2b** was detected in small amounts (^{19}F NMR) whereas cation **2a** and precursor **2** were in the solution in equal amounts. In contrast, dissolution of perfluoro-1-isopropylbenzocyclobutene (**3**) in $SbF_5–SO_2ClF$ gave mainly perfluoro-1-isopropylbenzocyclobuten-1-yl cation (**3b**) and small amounts of perfluoro-2-isopropylbenzocyclobuten-1-yl cation (**3a**) without precursor **3** (Scheme 1).

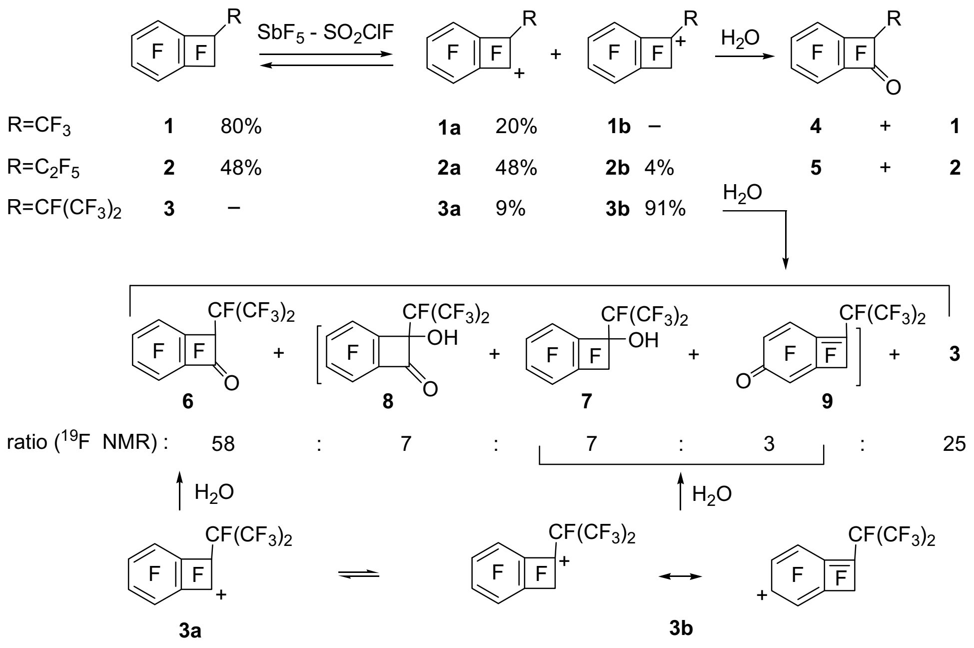
The treatment of the solutions of compounds **1**–**3** in $SbF_5–SO_2ClF$ with water led to perfluorinated 2-methyl- (**4**), 2-ethyl- (**5**) and 2-isopropyl- (**6**) benzocyclobuten-1-ones together with precursors **1**–**3**, respectively. In the last case the reaction mixture also seemed to contain perfluoro-1-hydroxy-1-isopropylbenzocyclobutene (**7**), perfluoro-2-hydroxy-2-isopropylbenzocyclobuten-1-one (**8**) and perfluoro-7-isopropylbicyclo[4.2.0]octa-1,4,6-trien-3-one (**9**) (Scheme 1). Compounds **7**–**9** were identified in the reaction mixture by ^{19}F NMR spectroscopy and GC–MS (compound **9**). It should be noted that compounds **7**, **8** were decomposed during GC, GC–MS and chromatography on a silica gel column.

It may be supposed that hydrolysis of cations **3a** and **3b** leads to compounds **6** and **7**, **9**, respectively. Hydroxyketone **8** apparently is a product of compound **6** or/and **7** transformations under the action of antimony pentafluoride and water during the aqueous treatment of the reaction mixture (cf. transformation of 3-dichloromethyleneperfluoroindan-1-yl cation to 3-dichloromethyleneperfluoroindan-1,2-dione [27] and transformation of perfluoro-1-(2-methylphenyl)-1-phenylprop-1-yl cation to perfluo-3-ethyl-3-phenylphthalide [28] during the aqueous treatment of SbF_5-solutions of reaction mixtures). In addition, the possibility of hydrolysis of dication generated from compound **3** cannot be excluded. Formation of precursor **3** during hydrolysis of the reaction mixture is evidently due to the process of fluoride ion capture by cations **3a,b** competing with hydrolysis (cf. hydrolysis of polyfluorobenzyl cations [7,8]).

When perfluoro-2-methyl-1-isopropylbenzocyclobutene (**10**) and perfluoro-1,2-diisopropylbenzocyclobutene (**11**) were dissolved in $SbF_5–SO_2ClF$, perfluorinated 2-methyl-1-isopropylbenzocyclobuten-1-yl (**12**) and 1,2-diisopropylbenzocyclobuten-1-yl (**13**) cations were generated in the absence of their precursors **10**, **11** (Scheme 2).

The treatment of the reaction mixtures with water resulted in forming perfluoro-7-isopropyl-8-methylbicyclo[4.2.0]octa-1,4,6-trien-3-one (**14**) and perfluoro-7,8-diisopropylbicyclo[4.2.0]octa-1,4,6-triene-3-one (**15**) together with precursors **10** and **11**, respectively. Apparently proximity of two bulky perfluoroalkyl groups hinders interaction of H_2O with the cationic centre in cations **12**, **13** (Scheme 2), as a result, H_2O reacts mainly with the more sterically accessible centre (*) of delocalized cations **12**, **13** to produce ketones **14** and **15**.

When perfluoro-1-methylindane (**16**) was dissolved in $SbF_5–SO_2ClF$, perfluoro-3-methylindan-1-yl cation (**16a**) was formed in small amounts (Scheme 3). Similarly, perfluoro-3-ethylindan-1-yl (**17a**) and perfluoro-1-ethylindan-1-yl (**17b**) cations were generated from perfluoro-1-ethylindane (**17**). In this case equilibrium was also shifted towards the precursor. In contrast, dissolution of perfluoro-1-isopropylindane (**18**) in $SbF_5–SO_2ClF$ led to perfluoro-



Scheme 1. Generation and hydrolysis of perfluoroalkylbenzocyclobutenyl cations.