Available online at www.sciencedirect.com

ScienceDirect

Journal of Fluorine Chemistry 128 (2007) 1058–1064

JOURNAL OF FLUORINE CHEMISTRY

www.elsevier.com/locate/fluor

Transformation of perfluorinated benzocycloalkenes and alkylbenzenes to their carbonyl derivatives under the action of CF_3COOH/SbF_5

Yaroslav V. Zonov, Victor M. Karpov *, Vyacheslav E. Platonov

N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Novosibirsk 630090, Russia

Received 24 April 2007; received in revised form 23 May 2007; accepted 29 May 2007
Available online 3 June 2007

Dedicated to Professor L.M. Yagupolskii, on the occasion of his 85th birthday.

Abstract

Perfluorinated benzocycloalkenes (benzocyclobutene, indan, tetralin), alkylbenzocycloalkenes and alkylbenzenes react with CF_3COOH/SbF_5 at 20–50 °C giving the corresponding carbonyl derivatives.

Keywords: Fluorinated; Benzocyclobutene; Indan; Tetralin; Alkylbenzene; Carbonyl derivatives; Trifluoroacetic acid; Antimony pentafluoride

---

1. Introduction

Perfluoroindan-1-one (**1**) and perfluoro-3-ethylindan-1-one (**2**) undergo skeletal transformations under the action of antimony pentafluoride [1,2]. Ketone **1** for this investigation was synthesized in a good yield in the reaction of perfluoroindan (**3**) with SiO_2/SbF_5 at 70 °C [1]. At the same time perfluoro-1-ethylindan (**4**) heated with SiO_2/SbF_5 at 75 °C and then treated with water, gives 4-carboxyperfluoro-3-methylisochromen-1-one. The process proceeds through the intermediate formation of ketone **2**, which was detected in the reaction mixture only in a small amount because ketone **2** undergoes skeletal transformations under the reaction conditions [2].

For the synthesis of compound **2** and other ketones, required for the investigation of their cationoid skeletal rearrangements, under milder conditions as compared with the reaction with SiO_2/SbF_5 it was worthwhile to try to replace SiO_2 by other sources of nucleophilic oxygen. For this purpose we have studied reactions of indan **3** with 2,2,3,3-tetrafluoropropanol, acetic and trifluoroacetic acids in the presence of SbF_5. This work also describes reactions of ethylindan **4** and other aromatic fluorocarbons with CF_3COOH/SbF_5.

2. Results and discussion

Reaction of indan **3** with 2,2,3,3-tetrafluoropropan-1-ol in an SbF_5 medium at 20–50 °C forms a solution of a salt of 1-(2,2,3,3-tetrafluoropropoxy)-perfluoroindan-1-yl cation (**5**). Hydrolysis of the latter gives indanon **1**. The reaction of compound **3** with CH_3COOH in the presence of SbF_5 at 50 °C forms ketone **1**. The reaction mixture also contains unchanged indan **3** (Scheme 1).

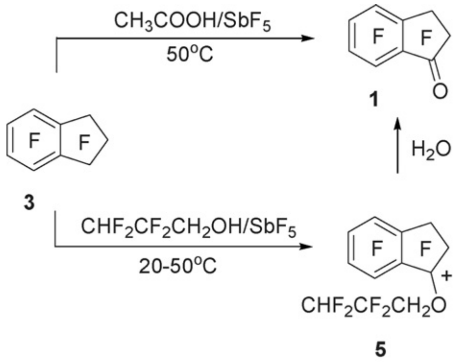
Compound **3** readily reacts with CF_3COOH in the presence of SbF_5 at room temperature to give indanone **1** in a high yield (Scheme 2). Reaction of compound **3** with CF_3COOH/SbF_5 at 50 °C gives ketone **1** together with perfluoroindan-1,3-dione (**6**). When the reaction temperature is raised to 95 °C perfluoro-3-methylenephthalide (**7**) is formed as a main product. The reaction mixture also contains ketone **1**, perfluoro-3-methylphthalide (**8**) and 4,5,6,7-tetrafluoro-3-trifluoromethylphthalide (**9**) (Scheme 2).

It is known that CF_3COOH in the presence of SbF_5 gives $H[SbF_5(OCOCF_3)]$ [3]. The formation of indanone **1** in the reaction of compound **3** with CF_3COOH/SbF_5 can be rationalized as shown in Scheme 2. Compound **3** with SbF_5 seems to generate perfluoroindan-1-yl cation (**3c**), which reacts with CF_3COOH to form perfluoro-1-acetoxyindan (**10**). Then perfluoro-1-acetoxyindan-1-yl cation (**10c**) produced from compound **10** is split into indanone **1** and the trifluoroacetyl cation. The latter adds fluoride anion to give trifluoroacetyl

---

* Corresponding author. Fax: +7 3832 34 4752.
E-mail address: karpov@nioch.nsc.ru (V.M. Karpov).

0022-1139/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2007.05.020



Scheme 1.

fluoride, which was trapped with sodium methylate as methyltrifluoroacetate.

The formation of indandione **6** can be represented in a similar way through the intermediate generation of perfluoroindan-3-one-1-yl cation (**1c**) according to Scheme 2. Compounds **7**, **8** and **9** are the products of transformations of indandione **6** under the reaction conditions similar to indandione **6** transformations under the action of SbF_5 [1] or HF/SbF_5 [4].

Taking into account the fact of higher reactivity of CF_3COOH/SbF_5 as compared with CH_3COOH/SbF_5 and $CHF_2CF_2CH_2OH/SbF_5$ in their reactions with indan **3** giving indanone **1**, for the synthesis of carbonyl derivatives of other perfluoroaromatic compounds, we have studied reactions of some aromatic fluorocarbons with CF_3COOH/SbF_5.

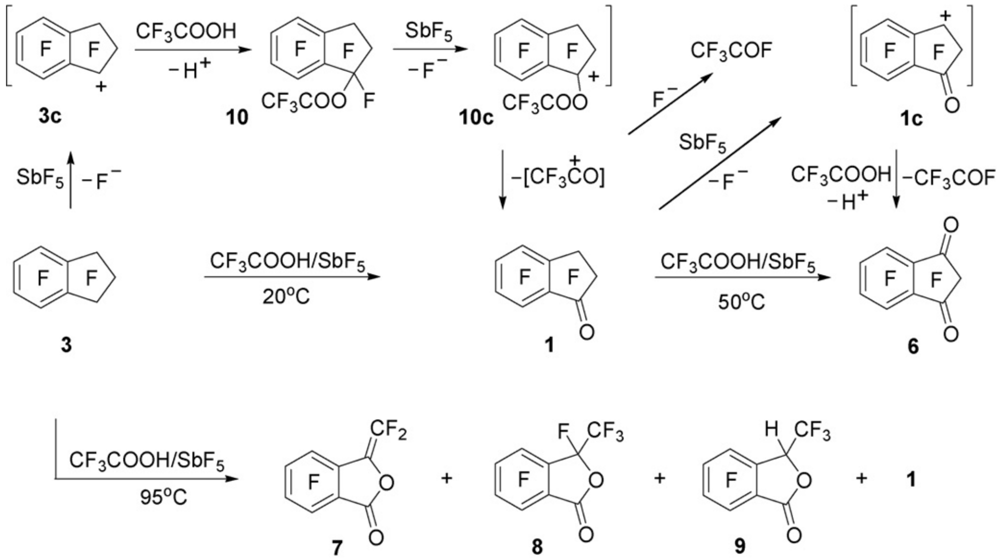
Perfluorotetralin (**11**) heated with CF_3COOH/SbF_5 at 50 °C gives perfluorotetralin-1-one (**12**). The reaction mixture also contains small amount of unchanged tetralin **11**. When the reaction temperature is raised to 95 °C, a mixture of ketone **12** and perfluorotetralin-1,4-dione (**13**) is obtained (Scheme 3).

The reaction of perfluorobenzocyclobutene (**14**) with CF_3COOH/SbF_5 proceeds readily at room temperature and gives perfluorobenzocyclobutenone (**15**) together with perfluorobenzocyclobutendione (**16**). Selective formation of ketone **15** can be achieved by the use of stoichiometric amounts of trifluoroacetic acid, whereas excess of CF_3COOH and heating up to 40 °C facilitate production of diketone **16**. When the reaction temperature is raised to 95 °C, after treatment of the reaction mixture with water, tetrafluorophthalic acid (**17**) is obtained as the only product (Scheme 3).

Perfluorinated 1-alkyl- and 1,1-dialkyl-benzocyclobutenes and indans also react with CF_3COOH/SbF_5 to give the corresponding benzocyclobutenones and indanones in a good yield. Thus, perfluorinated 1-methylbenzocyclobutene (**18**), 1-ethylbenzocyclobutene (**19**), 1,1-diethylbenzocyclobutene (**20**), 1-methylindan (**21**), 1-ethylindan (**4**), 1,1-dimethylindan (**22**), 1,1-diethylindan (**23**) are transformed to perfluorinated 2-methylbenzocyclobutenone (**24**), 2-ethylbenzocyclobutenone (**25**), 2,2-diethylbenzocyclobutenone (**26**), 3-methylindan-1-one (**27**), 3-ethylindan-1-one (**2**), 3,3-dimethylindan-1-one (**28**), 3,3-diethylindan-1-one (**29**), respectively (Scheme 4). These transformations smoothly proceed at room temperature and are not complicated by further skeletal rearrangements, in contrast to the reaction of indan **4** with SiO_2/SbF_5 [2].

Perfluoro-2-methylindan (**30**) reacts with CF_3COOH/SbF_5 at room temperature to give perfluoro-2-methylindan-1-one (**31**). Perfluoromethylindans containing a CF_3 group in the aromatic ring, heated with CF_3COOH/SbF_5 at 50 °C, form perfluoromethylindanones with a carbonyl group in the position meta to the CF_3 group. Thus perfluoro-4-methylindan (**32**) and perfluoro-5-methylindan (**33**) are transformed to perfluoro-4-methylindan-1-one (**34**) and perfluoro-6-methylindan-1-one (**35**), respectively. This is in accordance with the larger relative stability of the corresponding perfluoromethylindan-1-yl cations [5–7]. Perfluoro-3-methylindene (**36**) also reacts with CF_3COOH/SbF_5 to give perfluoro-3-methylinden-1-one (**37**) (Scheme 5).

The interaction of perfluorotoluene (**38**) and perfluoro-4-methyltoluene (**39**) with CF_3COOH/SbF_5, after treatment of the reaction mixture with water, leads to the formation of



Scheme 2.