



Carbonylation of polyfluorinated indans, tetralins and perfluoro-2,3-dihydrobenzofuran under the action of CO/SbF₅



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ABSTRACT

Polyfluorinated indans and tetralins are carbonylated under the action of CO/SbF₅ at room temperature and atmospheric pressure. Perfluoroindan and its 4-CF₃, 5-CF₃, 5-CH₃, 1,1-H,H derivatives add two CO molecules to form the corresponding dimethyl indan-1,1-dicarboxylates after methanolysis, and/or 1-hydroindan-1-carboxylic acids after hydrolysis. 1-X-Perfluoroindans (X=CF₃, C₂F₅, C₆F₅, H) and 1-X-perfluorotetralins (X=C₂F₅, C₆F₅) add one CO molecule at the 1-position to give the corresponding 1-carbonyl fluorides. Reaction of the latter with methanol gives methyl esters, whereas hydrolysis is accompanied by decarboxylation. Perfluoro-2,3-dihydrobenzofuran under the action of CO/SbF₅ gives both mono- and dicarbonylation products.

1. Introduction

Organo-fluorine compounds are essentially important for fundamental organic chemistry [1] and its applications, particularly to materials science, biomedicine and agriculture [1–3]. Therefore, development of new approaches for their synthesis is of obvious interest. Currently, in hydrocarbon chemistry, there are known many carbonylation reactions of alcohols, alkyl halides, alkenes etc. proceeding by CO addition to cations generated from these compounds in acidic systems and leading to the formation of carboxylic acid derivatives [4–6]. At the same time for polyfluorinated compounds, despite the variety of reactions of fluorinated cations, such carbonylation reactions have not been known until our recent reports [7,8]. Some examples of reverse reactions – the decarbonylation of fluorinated acyl halides under the action of Lewis acids were only observed [9–11].

We have found that perfluorinated benzocyclobutene and its alkyl and phenyl derivatives undergo carbonylation and four-membered ring opening or expansion under the action of carbon monoxide in the presence of SbF₅ resulting in formation of 2-arylalkenoic acid [7], isochromene [7,8] and indan-2-one derivatives [8]. In these reactions, irreversible four-membered ring transformations of the products of the initial CO addition promote the conversion of polyfluorobenzocyclobutenes into the final products. A number of fluorocarboxyl derivatives of indan-2-one obtained in these reactions apparently indicate the possibility of carbonylation of indan derivatives

under the reaction conditions. In the development of this research, in present article we report on the carbonylation of a number of polyfluorinated indans and tetralins and perfluoro-2,3-dihydrobenzofuran under the action of CO/SbF₅.

It should be pointed out that in hydrocarbon series it is known only a few examples of carbonylation of indan and tetralin derivatives at aliphatic ring and these reactions are catalyzed by palladium-phosphine complexes. Thus, carbonylation of 1-indanol and 1-tetralol gives 1- and 2-isomers of the corresponding methyl carboxylates [12], and carbonylation of 2-chlorotetralone gives methyl 1-oxotetralin-2-carboxylate [13]. At the same time, indan-1- and tetralin-1-carboxylic acid derivatives, including partially halogenated ones, have been reported to exhibit multiple biological activities [14,15].

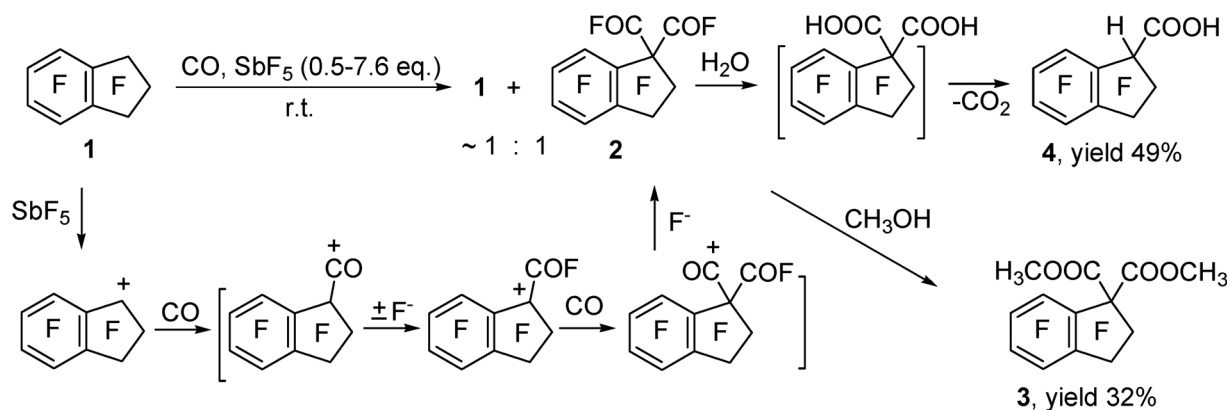
2. Results and discussion

2.1. Reactions of polyfluorinated indans and perfluoro-2,3-dihydrobenzofuran with CO–SbF₅

We have found that perfluoroindan (1) and a number of its derivatives react with carbon monoxide in the presence of SbF₅ at room temperature and atmospheric pressure. In contrast to the carbonylation of polyfluorobenzocyclobutenes the reaction of indan 1 with CO proceeds without transformations of the aliphatic ring. Indan 1 adds two CO molecules to form perfluoroindan-1,1-dicarbonyl difluoride (2)

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Scheme 1. Carbonylation of perfluoroindan.

(Scheme 1), but complete conversion is not achieved and the reaction mixture contains compounds **1** and **2** in about equal amounts. The increase in the reaction time from 5 to 28.5 h does not increase the degree of conversion. Variation of SbF_5 amount in the range of 0.5–7.6 mol equivalent also does not lead to significant changes in the result. When the reaction mixture is treated with methanol, compound **2** is transformed into dimethyl perfluoroindan-1,1-dicarboxylate (**3**), whereas the reaction with water gives 1-hydroperfluoroindan-1-carboxylic acid (**4**) which is a decarboxylation product of the corresponding 1,1-dicarboxylic acid.

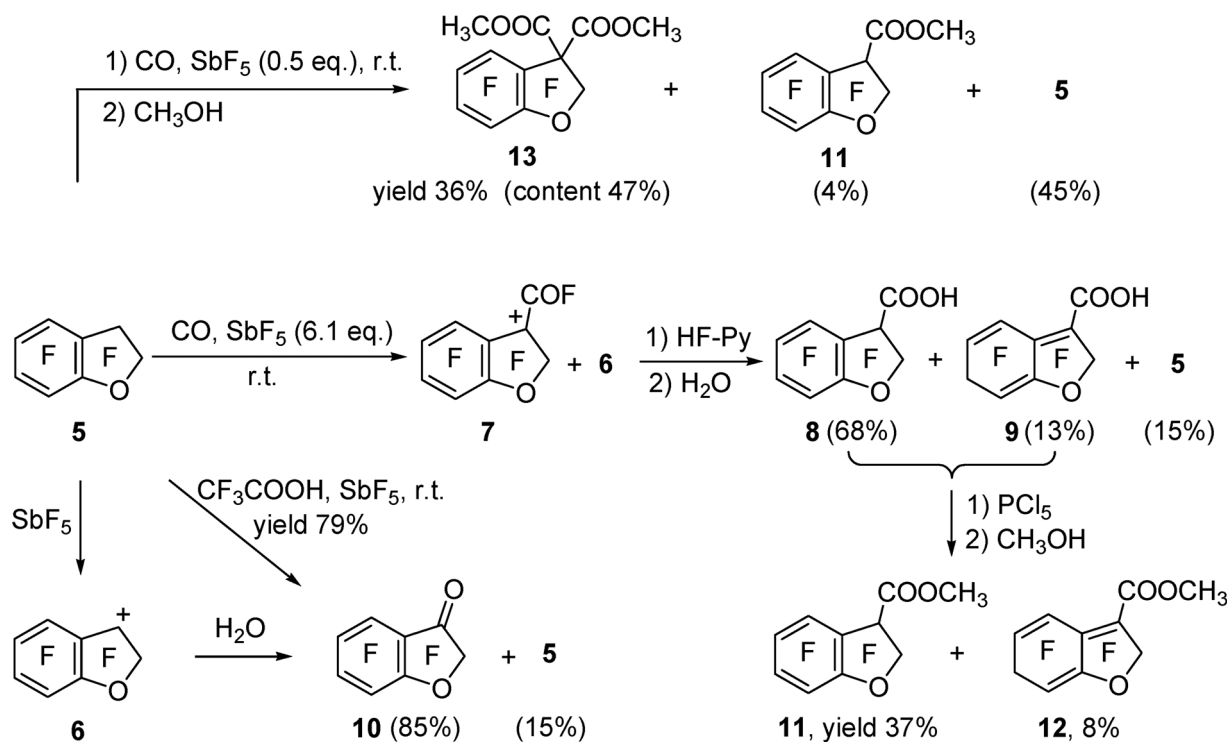
Heteroatomic analog of perfluoroindan (**1**) – perfluoro-2,3-dihydrobenzofuran (**5**), also reacts with CO-SbF_5 (Scheme 2). Under the action of excess of SbF_5 compound **5** is completely converted into a salt of perfluoro-2,3-dihydrobenzofuran-3-yl cation (**6**) which adds one CO molecule to form perfluoro-3-fluorocarbonyl-2,3-dihydrobenzofuran-3-yl cation (**7**). Treatment of the reaction mixture containing salts of cations **6** and **7** with HF-pyridine (Olah's reagent) and then with water gives mainly perfluoro-2,3-dihydrobenzofuran-3-carboxylic acid (**8**) along with perfluoro-2,6-dihydrobenzofuran-3-carboxylic acid (**9**) and the starting compound. Acids **8** and **9** are converted by treatment with

PCl_5 and then with methanol into corresponding methyl esters **11** and **12** which are separated chromatographically (Scheme 2).

Treatment of the salt of cation **6** with water leads to a mixture of perfluoro-2,3-dihydrobenzofuran-3-one (**10**) and compound **5**. Ketone **10** is also synthesized in the reaction of compound **5** with CF_3COOH and SbF_5 in a good yield.

Whereas in the excess of SbF_5 compound **5** undergoes monocarbonylation, in the presence of 0.5 mol equivalent of SbF_5 it adds two CO molecules to form, after methanolysis of the reaction mixture, dimethyl perfluoro-2,3-dihydrobenzofuran-3,3-dicarboxylate (**13**) along with the starting compound and only small amounts of monocarbonylation product **11** (Scheme 2).

Interaction of perfluorinated 4-methyl- (**14**) and 5-methylindans (**15**) with CO proceeds analogously to perfluoroindan (**1**) in the presence of excess of SbF_5 to give, after hydrolysis of the reaction mixtures, 1-hydroperfluoro-4-methylindan-1-carboxylic (**16**) and 1-hydroperfluoro-6-methylindan-1-carboxylic (**17**) acids (Scheme 3). The degree of conversion of indans **14** and **15** is lower than that of perfluoroindan (**1**) and does not increase with increase of the reaction time. The carbonylation proceeds regioselectively at the CF_2 group which is in the meta-position



Scheme 2. Carbonylation of perfluoro-2,3-dihydrobenzofuran.

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