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Transformations of perfluoroindan-1-one and perfluoroindan-1,3-dione in the HF–SbF_5 system

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

N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation. Fax: + 7 383 330 9752; e-mail: karpov@nioch.nsc.ru

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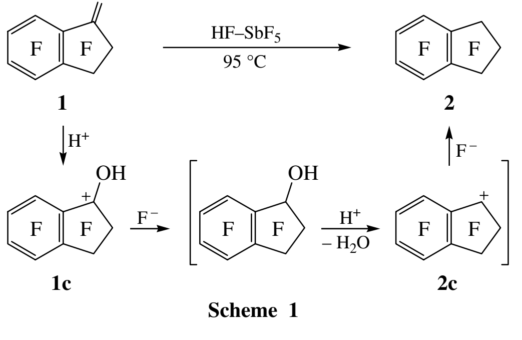
When heated with HF–SbF_5, perfluoroindan-1-one is converted into perfluoroindan, whereas perfluoroindan-1,3-dione isomerises into perfluoro-3-methylenephthalide.

When treated with antimony pentafluoride, perfluorinated ketones[1] and vinyl ketones[2] having a CF_3 group at the β-position to the carbonyl group undergo intramolecular cyclization to form derivatives of oxolane and 2,5-dihydrofuran, respectively. The heating of perfluoroindan-1-one **1** with SbF_5 and the treatment with water give perfluoro-2-ethylbenzoic acid together with the products of ketone **1** disproportionation, perfluoroindan **2** and perfluoroindan-1,3-dione **3**. The latter is transformed to perfluoro-3-methylphthalide **4**, for example, *via* intermediate perfluoro-3-methylenephthalide **5**.[3] The carbonyl groups of ketone **1**,[4] perfluorinated indan-2-one, 1-methylindan-2-one and 3-methylindenone[5] are involved in reactions with H_2O_2 in the HF–SbF_5 system to form six-membered oxygen-containing heterocyclic compounds. Here, we report the behaviour of ketones **1** and **3** in the HF–SbF_5 system.[†]

We found that, when acted upon by HF–SbF_5 at 95 °C, the carbonyl group of indanone **1** is converted into the difluoromethylene group to give indan **2**. The reaction mixture also contains unchanged ketone **1** (Scheme 1). There are no data that HF–SbF_5 was used as a fluorinating agent for the replacement of carbonyl oxygen by fluorine.[6,7]

A possible route for the transformation of ketone **1** to indan **2** is presented in Scheme 1. Apparently, compound **1** is protonated to give 1-hydroxyperfluoroindan-1-yl cation **1c** (^{19}F NMR), which adds a fluoride anion to form 1-hydroxyperfluoroindan. The protonation of the latter with the subsequent elimination of water leads to perfluoroindan-1-yl cation **2c**, which adds a fluoride anion to produce compound **2**.



Scheme 1

Indandione **3**, heated with HF–SbF_5 at 95 °C for 3 h, isomerises to phthalide **5**. The reaction mixture also contains small amounts of 4,5,6,7-tetrafluoro-3-trifluoromethylphthalide **6**, indanone **1** and unchanged compound **3** (Scheme 2). Phthalide **6** is the main product of the reaction of indandione **3** with HF–SbF_5 at 130 °C. Transformation of indandione **3** to phthalide **5** is the first example of isomerisation of fluorinated indandiones into 3-methylenephthalides.

The probable mechanism of the isomerisation of indandione **3** to phthalide **5** is shown in Scheme 2. The protonation of compound **3** gives 1-hydroxyperfluoroindan-3-on-1-yl cation **3c**. The five-membered ring cleavage in ion **3c** leads to cation **7**.

[†] *General procedure for the reactions of* **1** *and* **3** *with* HF–SbF_5. A mixture of compound **1** or **3** (2–3 mmol) with HF–SbF_5 was heated in a nickel bomb (10 ml) or in a Teflon closed container (20 ml). The mixture was poured into 5% hydrochloric acid and extracted with CH_2Cl_2. The extract was dried over $MgSO_4$. The solvent was evaporated to give a mixture of products. Contents (yields) of products in the reaction mixtures were established by ^{19}F NMR spectroscopy.

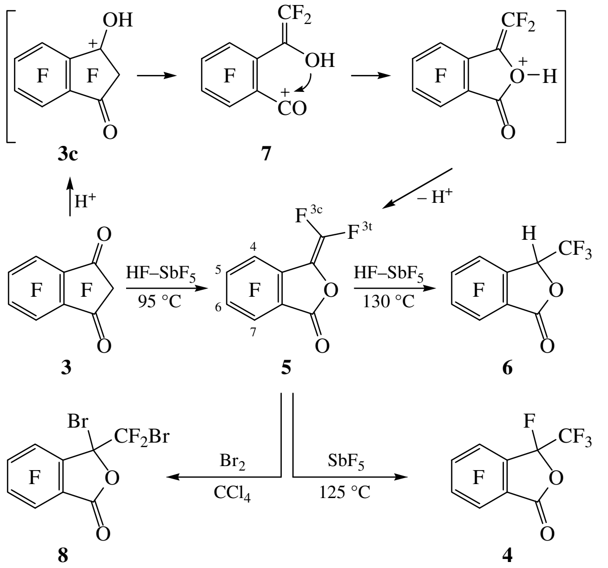
Indanone **1** (0.6 g) (molar ratio of **1**:HF:SbF_5 = 1:4.9:2.5) gave (95 °C, 43 h) 0.54 g of a mixture, which contained compounds **1** and **2** in the ratio 14:86 (yields, 12 and 72%).

Synthesis of **5**. Indandione **3** (0.8 g) (molar ratio of **3**:HF:SbF_5 = = 1:2.7:1.5) gave (95 °C, 3 h) 0.61 g of a mixture of compounds **1**, **3**, **5** (70% yield) and **6** in the ratio 2:5:92:1. Compound **5** is unstable under usual conditions.

Synthesis of **6**. Indandione **3** (0.77 g) (molar ratio of **3**:HF:SbF_5 = = 1:4.9:2.5) gave (130 °C, 11 h) 0.72 g (87% yield) of compound **6**.

Fluorination of **5**. Indandione **3** (0.84 g) (molar ratio of **3**:HF:SbF_5 = = 1:3.2:1.5) gave (95 °C, 3 h) 0.74 g of a mixture of compounds **1**, **3**, **5** and **6** in the ratio 11:8:79:2, which was heated at 125 °C for 3 h with 2.71 g of SbF_5 (molar ratio of **5**:SbF_5 = 1:3.8). A mixture (0.71 g), which contained 30% (22% yield) of 3-hydroxyperfluoro-3-methylphthalide,[3] 64% (47%) of **4**, 3% (2%) of **6** and 4% (2%) of perfluoro-2-ethylbenzoic acid, was obtained.[3]

Bromination of **5**. Compound **5** was prepared (95 °C, 3 h) from 1.44 g (5.7 mmol) of indandione **3** and HF–SbF_5 (molar ratio of **3**:HF:SbF_5 = = 1:2.7:1.5) and dissolved in 5 ml of CCl_4. Then 1.5 g (9.4 mmol) of Br_2 was added to the solution at ~20 °C and the mixture was kept at this temperature for 20 h. The mixture was washed with aqueous solutions of Na_2SO_3, then with $NaHCO_3$ and dried over $MgSO_4$. The solvent was distilled off to give 1.96 g (83% yield) of compound **8**, which was additionally purified by short-path distillation (90 °C, 3–4 Torr).



Scheme 2

Intramolecular cyclisation of the latter and subsequent deprotonation gives phthalide **5**.

When heated with SbF_5 at 125 °C, compound **5** is fluorinated to give phthalide **4**. Compound **5** reacts with bromine to form 3-bromo-3-(bromodifluoromethyl)-4,5,6,7-tetrafluorophthalide **8** (Scheme 2).

The structures of the compounds were fully supported by ^{1}H and ^{19}F NMR spectroscopy and mass spectrometry.‡

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‡ ^{19}F and ^{1}H NMR spectra were recorded on a Bruker WP-200 SY instrument (188.3 and 200 MHz, respectively). Chemical shifts are given in δ (ppm) downfield from C_6F_6 and TMS. The molecular masses of the compounds were determined by high-resolution mass spectrometry on a Finnigan Mat 8200 instrument (EI, 70 eV).

Cation **1c**: 0.26 g of **1** was dissolved in $HF–SbF_5$ (molar ratio of **1**:HF:SbF_5 = 1:4.9:2.5) and ^{19}F NMR spectrum of the solution was recorded, δ: 65.5 (ddd, 1F, F-5, $^{4}J_{5,7}$ 36 Hz, $^{3}J_{4,5}$ 19 Hz, $^{3}J_{5,6}$ 17 Hz), 59.4 (ddd, 1F, F-7, $^{4}J_{5,7}$ 36 Hz, $^{3}J_{6,7}$ 18 Hz, $^{5}J_{4,7}$ 13 Hz), 57.8 (d, 2F, F-3, $^{4}J_{3,4}$ 6 Hz), 47.9 (s, 2F, F-2), 34.4 (dddt, 1F, F-4, $^{3}J_{4,5}$ 19 Hz, $^{5}J_{4,7}$ 13 Hz, $^{4}J_{4,6}$ 12 Hz, $^{4}J_{3,4}$ 6 Hz), 27.5 (ddd, 1F, F-6, $^{3}J_{5,6}$ 17 Hz, $^{3}J_{6,7}$ 18 Hz, $^{4}J_{4,6}$ 12 Hz). Then, after treatment of the reaction mixture with water, compound **1** (0.23 g, yield 88%) was recovered. *Indanone* **1**: ^{19}F NMR (CH_2Cl_2) δ: 53.9 (m, 2F, F-3), 37.7 (t, 2F, F-2, $^{3}J_{2,3}$ 3 Hz), 30.5 (ddd, 1F, F-7, $^{3}J_{6,7}$ 20 Hz, $^{5}J_{4,7}$ 18 Hz, $^{4}J_{5,7}$ 13 Hz), 28.2 (ddd, 1F, F-5, $^{3}J_{4,5}$ 20 Hz, $^{3}J_{5,6}$ 18 Hz, $^{4}J_{5,7}$ 13 Hz), 26.4 (dddt, 1F, F-4, $^{3}J_{4,5}$ 20 Hz, $^{5}J_{4,7}$ 18 Hz, $^{4}J_{4,6}$ 9 Hz, $^{4}J_{3,4}$ 7 Hz), 20.3 (ddd, 1F, F-6, $^{3}J_{6,7}$ 20 Hz, $^{3}J_{5,6}$ 18 Hz, $^{4}J_{4,6}$ 9 Hz).

Perfluoro-3-methylenephthalide **5**: ^{19}F NMR (CH_2Cl_2) δ: 78.1 (dddd, 1F, F-3t, $^{2}J_{3c,3t}$ 33 Hz, $^{7}J_{3t,6}$ 8 Hz, $^{5}J_{3t,4}$ 7 Hz, $^{6}J_{3t,5}$ 3 Hz), 63.8 (ddddd, 1F, F-3c, $^{5}J_{3c,4}$ 54 Hz, $^{2}J_{3c,3t}$ 33 Hz, $^{7}J_{3c,6}$ 6 Hz, $^{6}J_{3c,5}$ 2 Hz, $^{6}J_{3c,7}$ 2 Hz), 25.6 (ddddd, 1F, F-4, $^{5}J_{3c,4}$ 54 Hz, $^{3}J_{4,5}$ 19 Hz, $^{5}J_{4,7}$ 19 Hz, $^{5}J_{3t,4}$ 7 Hz, $^{4}J_{4,6}$ 4 Hz), 24.8 (dddd, 1F, F-7, $^{3}J_{6,7}$ 20 Hz, $^{5}J_{4,7}$ 19 Hz, $^{4}J_{5,7}$ 10 Hz, $^{6}J_{3c,7}$ 2 Hz), 21.1 (ddddd, 1F, F-5, $^{3}J_{4,5}$ 19 Hz, $^{3}J_{5,6}$ 18 Hz, $^{4}J_{5,7}$ 10 Hz, $^{6}J_{3t,5}$ 3 Hz, $^{6}J_{3c,5}$ 2 Hz), 12.7 (ddddd, 1F, F-6, $^{3}J_{6,7}$ 20 Hz, $^{3}J_{5,6}$ 18 Hz, $^{7}J_{3t,6}$ 8 Hz, $^{7}J_{3c,6}$ 6 Hz, $^{4}J_{4,6}$ 4 Hz). IR (CCl_4, ν/cm^{-1}): 1823, 1809 (C=O), 1734 ($C=CF_2$), 1526, 1497 (C_6F_4).

4,5,6,7-Tetrafluoro-3-trifluoromethylphthalide **6**: mp 93.5–94.5 °C (hexane). ^{1}H NMR (CCl_4) δ: 5.77 (q, H-3, $^{3}J_{H–CF_3}$ 5 Hz). ^{19}F NMR (CCl_4) δ: 85.2 (dd, 3F, CF_3, $^{3}J_{H–CF_3}$ 5 Hz, $^{5}J_{CF_3–F(4)}$ 14 Hz), 26.2 (ddd, 1F, F-7, $^{3}J_{6,7}$ 20 Hz, $^{5}J_{4,7}$ 19 Hz, $^{4}J_{5,7}$ 10 Hz), 24.0 (ddqd, 1F, F-4, $^{3}J_{4,5}$ 20 Hz, $^{5}J_{4,7}$ 19 Hz, $^{5}J_{CF_3–F(4)}$ 14 Hz, $^{4}J_{4,6}$ 6 Hz), 20.9 (ddd, 1F, F-5, $^{3}J_{4,5}$ 20 Hz, $^{3}J_{5,6}$ 18 Hz, $^{4}J_{5,7}$ 10 Hz), 14.9 (ddd, 1F, F-6, $^{3}J_{6,7}$ 20 Hz, $^{3}J_{5,6}$ 18 Hz, $^{4}J_{4,6}$ 6 Hz). IR (CCl_4, ν/cm^{-1}): 2965 (CH), 1823, 1796 (C=O), 1520, 1504 (C_6F_4). HRMS, *m/z*: 273.9855 (M^+; calc. for $C_9HF_7O_2$ 273.9865).

3-Bromo-3-(bromodifluoromethyl)-4,5,6,7-tetrafluorophthalide **8**: ^{19}F NMR (CH_2Cl_2) δ: 107.8 (dd, $1F_A$, CF_2Br, $^{2}J_{A,B}$ 170 Hz, $^{5}J_{A,4}$ 32 Hz), 106.7 (dd, $1F_B$, CF_2Br, $^{2}J_{A,B}$ 170 Hz, $^{5}J_{B,4}$ 13 Hz), 29.9 (ddddd, 1F, F-4, $^{5}J_{A,4}$ 32 Hz, $^{3}J_{4,5}$ 20 Hz, $^{5}J_{4,7}$ 19 Hz, $^{5}J_{B,4}$ 13 Hz, $^{4}J_{4,6}$ 8 Hz), 27.5 (ddd, 1F, F-7, $^{3}J_{6,7}$ 20 Hz, $^{5}J_{4,7}$ 19 Hz, $^{4}J_{5,7}$ 11 Hz), 24.3 (ddd, 1F, F-5, $^{3}J_{4,5}$ 20 Hz, $^{3}J_{5,6}$ 18 Hz, $^{4}J_{5,7}$ 11 Hz), 17.8 (ddd, 1F, F-6, $^{3}J_{6,7}$ 20 Hz, $^{3}J_{5,6}$ 18 Hz, $^{4}J_{4,6}$ 8 Hz). HRMS, *m/z*: 332.8945 (M^+ – Br; calc. for $C_9BrF_6O_2$ 332.8986). Found (%): Br, 38.8; F, 27.8. Calc. for $C_9Br_2F_6O_2$ (%): Br, 38.6; F, 27.5.