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Journal of Fluorine Chemistry 128 (2007) 714–717
JOURNAL OF FLUORINE CHEMISTRY
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The high-temperature alicyclic ring contraction of 1,1-dichloroperfluorotetralin and the alicyclic ring opening of 1,1-dichloroperfluorobenzocyclobutene

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Received 23 January 2007; received in revised form 21 February 2007; accepted 21 February 2007
Available online 25 February 2007

Dedicated to the Centenary of Academician, Professor I.L. Knunyants.

Abstract

The pyrolysis of 1,1-dichloroperfluorotetralin (**4**) in a stream of argon gives a mixture contained perfluoro-1-methyleneindan (**1**), perfluoro-3-methylindene (**6**), 1,1-dichloroperfluoroindan (**2**) and perfluoroindene (**7**), while copyrolysis of tetralin **4** with $CHClF_2$ gives a mixture of compounds **1**, **6** in the absence of compounds **2** and **7**. 1-Chloro-2-(1-chloro-2,2-difluorovinyl)-3,4,5,6-tetrafluorobenzene (**12**) is formed in the pyrolysis of 1,1-dichloroperfluorobenzocyclobutene (**5**) in a stream of argon as well as in a stream of $CHClF_2$.

Keywords: Fluorinated; Tetralin; Benzocyclobutene; Pyrolysis; Ring contraction; Ring opening

1. Introduction

Copyrolysis of α,α-dichloropolyfluoroalkylbenzenes [1,2] and 1,1-dichloropolyfluoroindans [3] with $CHClF_2$ as a source of difluorocarbene [4,5] is known to give polyfluorostyrenes and polyfluoro-1-methyleneindans, respectively. It has been shown that formation of perfluoro-1-methyleneindan (**1**) in the reaction of 1,1-dichloroperfluoroindan (**2**) with $CHClF_2$ can proceed by way of difluorocarbene insertion into C–Cl bond of compound **2**, giving 1-chloro-1-(chlorodifluoromethyl)perfluoroindan (**3**), with subsequent dechlorination of the latter [3] (Scheme 1).

It was interesting to investigate high-temperature reactions of other polyfluorinated 1,1-dichlorobenzocycloalkenes with $CHClF_2$ in order to study the effect of the alicyclic ring size on the route of polyfluorobenzocycloalkenes transformations. This work describes the copyrolysis of 1,1-dichloroperfluorotetralin (**4**) and 1,1-dichloroperfluorobenzocyclobutene (**5**) with $CHClF_2$, as well as their high-temperature behaviour in a stream of argon.

2. Results and discussion

It has been shown that in copyrolysis of tetralin **4** with $CHClF_2$ the main reaction product is compound **1**. The reaction mixture also contains small amount of perfluoro-3-methylindene (**6**), which is a product of isomerization of compound **1** under the reaction conditions [3], together with unidentified impurities (Scheme 2). The formation of compounds **1** and **6** takes place also in the pyrolysis of tetralin **4** in a stream of argon. But in this case the reaction mixture contains also indan **2** and perfluoroindene (**7**).

Some possible routes for the transformation of tetralin **4** to compound **1** can be formulated as shown in Scheme 3. One can suppose that compound **4** undergoes homolytical transformations including generation of 1-chloroperfluorotetralin-1-yl radical (**8**) with its subsequent β-cleavage similar to [6] and the formation of 2-[2-(1-chloro-2,2-difluorovinyl)tetrafluorophenyl]tetrafluoroethyl radical (**9**) (Scheme 3). The latter can undergo the intramolecular cyclization giving radical **10**. A concert mechanism is also likely. The loss of the chlorine atom

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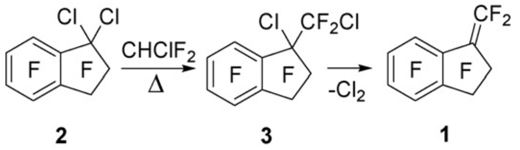
doi:10.1016/j.jfluchem.2007.02.015



Scheme 1.

from radical **10** gives compound **1**. One cannot also exclude the possibility of compound **1** being formed by generation of carbene **11** with subsequent alicyclic ring contraction of the latter. It should be noted that migration of perfluoroalkyl group is known for carbenes [7] as well as for radicals [8].

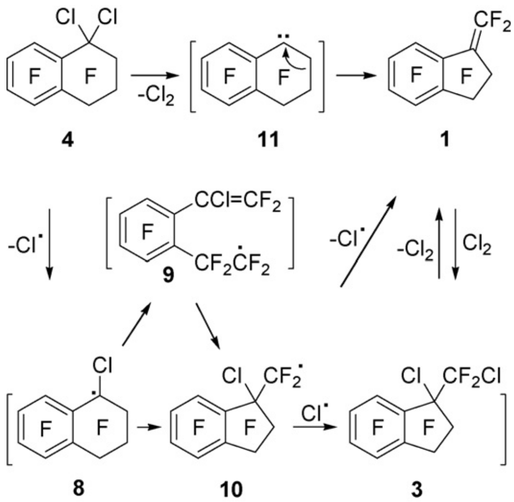
When the reaction is provided under argon in the absence of acceptors of chlorine (:CF$_2$, CF$_2$=CF$_2$, which are pyrolysis products of CHClF$_2$ [4,5]), a chlorination of radical **10** or/and compound **1** can form product **3**. The high-temperature transformations of the latter apparently give compounds **1**, **2**, **6**, **7**.

This explanation is in accordance with the fact that mixtures of compounds **1**, **6** and **1**, **2**, **6**, **7**, similar to that for tetralin **4**, are formed in the copyrolysis of compound **3** with CHClF$_2$ [3] and in its high-temperature reaction in a stream of argon, respectively (Scheme 2).

Copyrolysis of compound **5** with CHClF$_2$ also gives methyleneindan **1**, but the main product of the reaction is 1-chloro-2-(1-chloro-2,2-difluorovinyl)-3,4,5,6-tetrafluorobenzene (**12**). The latter is also formed in the pyrolysis of compound **5** in a stream of argon (Scheme 4).

One can assume the possibility of compound **1** being formed by intermediate formation of indan **2** with subsequent reaction of the latter with CHClF$_2$. But this route is improbable because compound **3**, which is formed in the reaction of indan **2** with CHClF$_2$ at 570 °C [3], was not identified in the reaction mixture obtained in copyrolysis of compound **5** with CHClF$_2$ at this temperature.

It may be suggested that compound **1** is formed by intermediate formation of perfluoro-1-methylenebenzocyclobutene (**13**) with subsequent four-membered ring expansion of the latter under the action of difluorocarbene (Scheme 4). A possibility of high-temperature expansion of the four-membered ring of polyfluorinated benzocyclobutenes to the five-membered one under the action of difluorocarbene was discussed, for example, in work [9]. In addition, one cannot also exclude the possibility of compound **1** formation via intermediate perfluorospiro[benzocyclobutene-1,1′-cyclopropane] (**14**), the product of a cycloaddition of difluorocarbene to the double bond of compound **13** (Scheme 4). Spiro-derivative **14** could be further converted into diradical **15**, similar to that discussed for perfluorospiro[indan-1,1′-cyclopropane] [10]. Four-membered ring opening of diradical **15** and subsequent cyclization of diradical **16** lead to compound **1**. The formation of compound **13** from benzocyclobutene **5** may be represented similar to that of compound **1** from indan **2** and CHClF$_2$ [3].



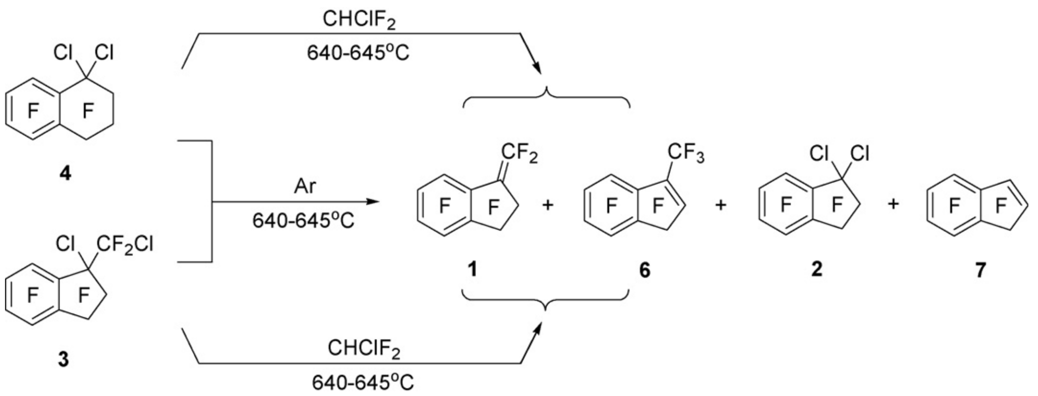
Scheme 3.

One of possible routes for the transformation of compound **5** to styrene **12** can be formulated as shown in Scheme 5.

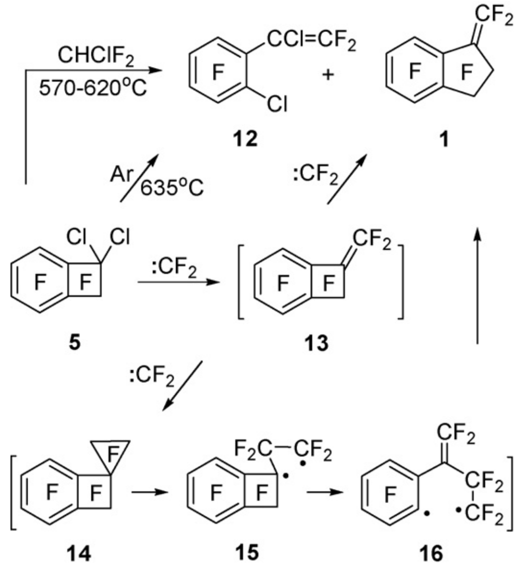
One can assume that compound **5** undergoes intramolecular isomerization into intermediate **17** with subsequent opening of the four-membered ring of the latter. A concert mechanism is also likely.

It should be noted that the reaction inverse to that discussed above proceeds under photolysis of polyfluorostyrenes giving polyfluorobenzocyclobutenes (Scheme 5) [11].

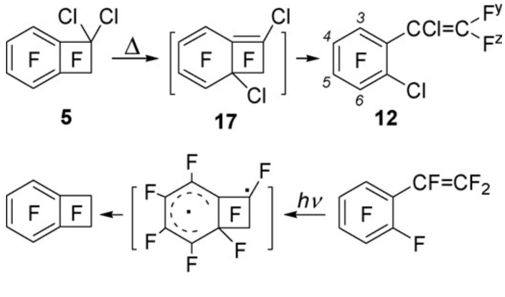
Compound **4**, required for the investigation of high-temperature reactions, was synthesized under the heating of



Scheme 2.



Scheme 4.

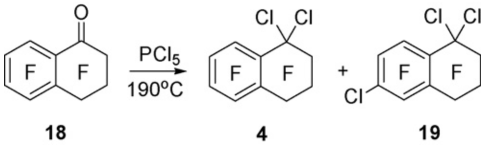


Scheme 5.

perfluoro-3,4-dihydronaphthalen-1(2H)-one (**18**) with PCl_5 (Scheme 6). Other reaction product was 1,1,6-trichloroperfluorotetralin (**19**) together with unidentified impurities.

3. Experimental

IR spectrum of styrene **12** was taken on a Bruker Vector 22 IR spectrophotometer. ^{19}F NMR spectra of compounds were recorded on a Bruker WP-200 SY instrument (188.3 MHz). Chemical shifts are given in δ (ppm) from CCl_3F; C_6F_6 (−162.9 ppm from CCl_3F) was used as internal standard. The molecular masses of the compounds were determined by high-resolution mass spectrometry on a Finnigan Mat 8200 instrument (EI 70 eV). Contents of products in the reaction mixtures were established by GLC-method and ^{19}F NMR spectroscopic data.



Scheme 6.

The structures of the compounds were established by elemental analysis, HRMS and spectral characteristics. Assignment of signals in the ^{19}F NMR spectra was made on the basis of chemical shifts of the signals, their fine structure and integral intensities. The spectrum of compound **11** is in agreement with spectra of others polyfluorostyrenes [2,12,13]. Compounds **1** [3], **2** [14], **6** [3], **7** [3,15] were identified by comparison of the ^{19}F NMR data with those for authentic samples.

*3.1. Reaction of perfluoro-3,4-dihydronaphthalen-1(2H)-one (**18**) with PCl_5*

A mixture of 5.9 g (18.1 mmol) of compound **18** with 12.8 g (61.3 mmol) of PCl_5 was heated in a sealed ampoule at 190 °C for 7 h. The contents were transferred into water. The organic layer was dried over $MgSO_4$ to give a mixture (7 g), which contained (GLC and ^{19}F NMR) 72% (yield 73%) of compound **4** and 10% (10%) of **19** together with unidentified impurities. Chlorotetralins **4** and **19** were isolated by preparative GLC (170 °C, SKTFT-50 on chromaton N, N_2).

1,1-Dichloroperfluorotetralin (**4**): liquid. NMR ^{19}F ($CHCl_3$): δ −106.5 (2F, F-4), −119.7 (2F, F-2), −127.5 (1F, F-8), −131.5 (2F, F-3), −136.7 (1F, F-5), −144.7 (1F, F-7), −147.0 (1F, F-6); $J_{4,5} = 21$ Hz, $J_{4,6} = 1$ Hz, $J_{4,7} = 2$ Hz, $J_{4,8} = 1$ Hz, $J_{5,6} = 21$ Hz, $J_{5,7} = 9$ Hz, $J_{5,8} = 11$ Hz, $J_{6,7} = 21$ Hz, $J_{6,8} = 10$ Hz, $J_{7,8} = 21$ Hz. Anal. Calcd for $C_{10}Cl_2F_{10}$: M 379.9217; C, 31.5; Cl, 18.6; F, 49.9%. Found: HRMS *m/z*, 379.9214 (M^+); C, 31.5; Cl, 18.6; F, 50.4%.

1,1,6-Trichloroperfluorotetralin(**19**): liquid. NMR ^{19}F ($CHCl_3$): δ −106.8 (2F, F-4), −114.3 (1F, F-5), −119.7 (2F, F-2), −123.9 (1F, F-7), −129.1 (1F, F-8), −131.3 (2F, F-3); $J_{4,5} = 22$ Hz, $J_{4,7} = 2$ Hz, $J_{4,8} = 1$ Hz, $J_{5,7} = 5$ Hz, $J_{5,8} = 13$ Hz, $J_{7,8} = 20$ Hz. Anal. Calcd for $C_{10}Cl_3F_9$: M 395.8922; C, 30.2; Cl, 26.8; F, 43.0%. Found: HRMS *m/z*, 395.8919 (M^+); C, 30.5; Cl, 26.6; F, 43.0%.

*3.2. Copyrolysis of compound **4** with $CHClF_2$*

Compound **4** (8.61 g) was passed through quartz tube (400 mm × 20 mm) at 640–645 °C in a stream of $CHClF_2$ (15 l/h) for 45 min. Distillation with steam gave 6.2 g of a mixture (dried over $MgSO_4$), which contained 57% of methyleneindan **1** and 9% of methylindene **6**.

*3.3. Pyrolysis of compounds **3** and **4***

1. By following a similar procedure, from 1.3 g of compound **4** in a stream of argon (15 l/h) at 640–645 °C (7 min) 0.85 g of a mixture were obtained, which contained compounds **1** (16%), **2** (12%), **6** (29%) and **7** (5%).
2. Analogously to procedure (1), from 2 g of compound **3** in a stream of argon (15 l/h) at 640–645 °C (10 min) 1.26 g of a mixture were obtained, which contained compounds **1** (17%), **2** (19%), **6** (18%), **7** (13%).

3. Copyrolysis of compound **3** with $CHClF_2$ gave a mixture, which contained compounds **1** (69%) and **6** (4%) [3].

3.4. Pyrolysis of 1,1-dichloroperfluorobenzocyclobutene (5)

By following a procedure similar to that described above, from 2 g of compound **5** [9] in a stream of argon at 630–635 °C (10 min) 1.46 g of a mixture were obtained, which contained 81% of compound **12**. Analytical sample of compound **12** was isolated by preparative GLC (140 °C, SKTFT-50 on chromaton N, N_2).

1-Chloro-2-(1-chloro-2,2-difluorovinyl)-3,4,5,6-tetrafluorobenzene (**12**): liquid. IR (CCl_4) ν, cm^{-1}: 1745 ($CCl = CF_2$); 1630, 1514, 1477 (fluorinated aromatic ring). NMR ^{19}F ($CHCl_3$): δ −83.0 (1F, F-Y), −83.9 (1F, F-Z), −135.5 (1F, F-3), −137.0 (1F, F-6), −150.5 (1F, F-5), −156.1 (1F, F-4); $J_{Y,Z} = 21$ Hz, $J_{Y,3} = 2$ Hz, $J_{Z,3} = 3$ Hz, $J_{3,4} = 22$ Hz, $J_{3,5} = 5$ Hz, $J_{3,6} = 10$ Hz, $J_{4,5} = 20$ Hz, $J_{4,6} = 3$ Hz, $J_{5,6} = 21$ Hz. Anal. Calcd for $C_8Cl_2F_6$: M 279.9281; C, 34.2; Cl, 25.2; F, 40.6%. Found: HRMS *m/z*, 279.9286 (M^+); C, 34.6; Cl, 25.4; F, 40.4%.

3.5. Copyrolysis of compound 5 with $CHClF_2$

1. By following a procedure similar to that described above, from 1.5 g of compound **5** and $CHClF_2$ at 620 °C (8 min) 0.91 g of a mixture were obtained, which contained compounds **1** (9%) and **12** (70%).
2. Analogously to procedure (1), from 1.1 g of compound **5** and $CHClF_2$ at 570 °C (6 min) 0.6 g of a mixture were obtained, which contained compounds **1** (11%), **5** (27%) and **12** (45%).

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