Letters to the Editor

Three-membered ring opening in perfluoro-1,1a,6,6a-tetrahydrocyclopropa[*a*]indene and its 1a-trifluoromethyl derivative under the action of SbF_5

V. M. Karpov and V. E. Platonov*

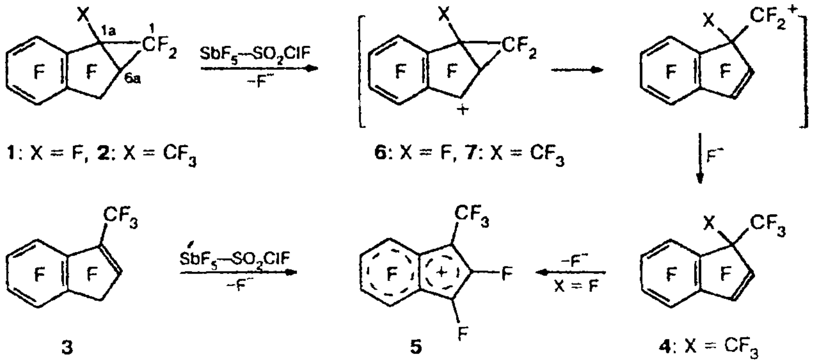
*Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences,
9 prosp. akad. Lavrent'eva, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383 2) 35 4752*

Perfluoro-1,1a,6,6a-tetrahydrocyclopropa[*a*]indene (**1**) is mainly isomerized upon thermolysis into perfluoro-2-methylindene,[1] and perfluoro-1a-methyl-1,1a,6,6a-tetrahydrocyclopropa[*a*]indene (**2**) eliminates difluorocarbene $:CF_2$ to give perfluoro-3-methylindene (**3**).[2] Bromination of **1** and **2** results[2] in the products of addition of Br_2 and is accompanied by the C(1)—C(1a) bond cleavage in **2** and C(1)—C(1a) and C(1a)—C(6a) bond cleavage in **1**.

To the contrary, we have shown that in compounds **1** and **2** another bond is cleaved under the action of SbF_5, namely, C(1)—C(6a). For example, in a SbF_5—SO_2ClF system, compound **2** is isomerized to perfluoro-1,1-dimethylindene (**4**), and compound **1** gives a salt of perfluoro-1-methylindene cation (**5**). The reaction most likely occurs *via* the intermediate formation of cations **6** and **7** (*cf.* Ref. 3) according to Scheme 1.

Ion **5** is also generated from perfluoromethylindene **3** and SbF_5. It is noteworthy that hydrocarbon analogs of cations **6** and **7** in acidic media behave in a different way: they are isomerized to 1*H*-naphthalenonium[4] and 4-methyl-1*H*-naphthalenonium ions,[5] respectively.

Scheme 1



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Compound **2** (0.14 g) was added to a solution of SbF_5 (0.34 g) in SO_2ClF at −50 °C (molar ratio **2** : SbF_5 = 1 : 4) with stirring. The ^{19}F NMR spectrum of the mixture (−40 °C, 0 °C) contained only broadened signals of antimony fluorides. The mixture was kept at −0 °C for 1 h and poured in water. The product was isolated by distillation (90 °C, 40 Torr), the yield of **4** was 0.1 g.

Similarly, product **4** (0.54 g) was obtained from compound **2** (0.56 g) and SbF_5 (0.67 g) (1 : 2) in SO_2ClF. Found: molecular mass 359.9841. $C_{11}F_{12}$. Calculated: molecular mass 359.9808. IR (CCl_4), v/cm^{-1}: 1726 (C=C); 1515, 1500 (fluorinated aromatic ring); 1442. UV (heptane), λ_{max}/nm (log ε): 254 (3.73), 260 sh (3.63), 290 (3.38), 296 sh (3.34). ^{19}F (CCl_4, internal standard C_6F_6), δ: 95.9 (2 *C*F(1)$_3$); 29.5 (F(7)); 20.8 (F(3)); 17.2 (F(2)); 16.2 (F(4)); 14.8 (F(5)); 10.7 (F(6)).

A solution of compound **1** (0.074 g) and SbF_5 (0.31 g) (1 : 6) in SO_2ClF was prepared at −70 °C. The ^{19}F NMR (−60 °C) coincided with the spectrum of a solution of the salt of cation **5** generated from **3**. ^{19}F NMR of product **5** (−40 °C, C_6F_6), δ: 168.5 (F(3)); 110.5 (F(4)); 97.3 (*C*F(1)$_3$); 79.5 (F(6)); 66.2 (F(7)); 40.2 (F(2)); 20.7 (F(5)). Hydrolysis of a solution of **3** in SbF_5 results in the formation of perfluoro-3-methylindenone.[6]

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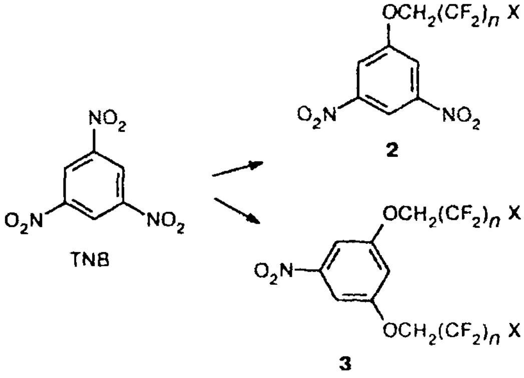
Reaction of polyfluorinated alcohols with 1,3,5-trinitrobenzene and its analogs

S. A. Shevelev, M. D. Dutov, M. A. Korolev, O. Yu. Sapozhnikov, and A. L. Rusanov*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 117913 Moscow, Russian Federation.
Fax: +7 (095) 135 5328. E-mail: shevelev@cacr.ioc.ac.ru

The addition of a nucleophile to the aromatic ring (at *ortho*- and *para*-positions to the nitro groups) to form stable anionic σ-complex is a standard result of reactions of nucleophiles with 1,3,5-trinitrobenzene (TNB) and its analogs with *meta*-arranged nitro groups; the main regularities of these processes are well studied.[1] The possibilities and conditions of substitution of the nitro groups in TNB under the action of nucleophiles are considerably less known.[2] Systematic studies in this field with TNB[3,4] and its analogs[5,6] as substrates (see also Ref. 7) have been started only recently using phenols and thiophenols as the nucleophiles.

We have found the conditions in which one or two nitro groups in TNB are substituted under the action of polyfluorinated alcohols $X(CF_2)_nCH_2OH$ (**1**) (X = F, *n* = 1 (**1a**); X = H, *n* = 2 (**1b**), 4 (**1c**), 6 (**1d**), and 8 (**1e**)) to form previously unknown 1-polyfluoroalkoxy-3,5-dinitrobenzenes (**2**) and 1,3-bis(polyfluoroalkoxy)-



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