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), ν/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 *CF*(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 (*CF*(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

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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)-

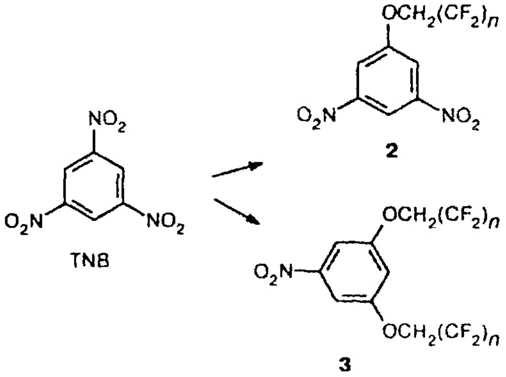

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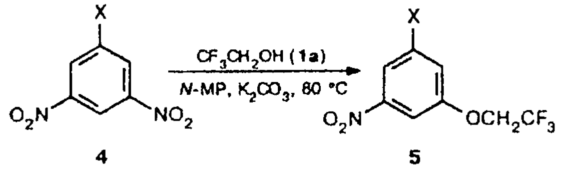
Table 1. Yields and melting points of products **2**, **3**, and **5**

Compound (X, *n*)	Yield (%)	M.p./°C
2a (F, 1)	81	49—50
2b (H, 2)	76	75—76
2c (H, 4)	66	36—37
2d (H, 6)	75	30—32
2e (H, 8)	69	51—53
3a (H, 2)	60	78—79
3b (H, 6)	53	39—41
5a (CF_3)	46	37—39
5b ($PhSO_2$)	69	133—135

5-nitrobenzenes (**3**), respectively. The reaction occurs smoothly in *N*-methylpyrrolidone (*N*-MP) in the presence of solid K_2CO_3 at 80 °C for the substitution of one nitro group (equimolar ratio of reagents) and at 140 °C for the substitution of two nitro groups (for **1b** and **1d** with the formation of **3a** and **3b**, using double molar amounts of **1** and K_2CO_3) during several hours (until complete conversion of TNB) (Table 1).

The reaction conditions are specific for **1** ($pK_{a(H_2O)} \approx$ 12—13 (see Ref. 8); under these conditions, unsubstituted aliphatic and acyclic alcohols ($pK_{a(H_2O)} \approx 16$ (see Ref. 9) either do not give products at all, or their yields are very small. Using the reaction of **1a** with 1-X-3,5-dinitrobenzenes (X = CF_3 (**4a**), $PhSO_2$ (**4b**)) as an example, we have shown that in these compounds the nitro group can be substituted by the polyfluoroalkoxyl fragment to form **5a** and **5b**, respectively; no products of the substitution of the groups X are formed (Table 1).



X = CF_3 (**4a**, **5a**), $PhSO_2$ (**4b**, **5b**)

Preliminary qualitative estimate of the reaction rates (at 80 °C, in *N*-MP) of **1a** with 1-X-3,5-dinitrobenzenes and TNB in the presence of K_2CO_3 (by determining the time of conversion of the starting compounds and accumulation of the products of substitution of the nitro group under identical conditions, ^{1}H NMR data) indicate the following series of activation of substitution under the action of X: $NO_2 > PhSO_2 > CF_3$. This corresponds to a decrease in the electron-withdrawing character of substituents, which is reflected in this case by the aromatic *meta*-constants of substituents (σ_m) for the NO_2, $PhSO_2$, and CF_3 groups.[10]

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