

Use of Polytetrafluoroethylene in Thermal Reactions

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Abstract

Pyrolysis reactions of polytetrafluoroethylene (PTFE) proceeding under various conditions and giving rise to perfluoroolefins and perfluorocyclobutane together with perfluoroalkanes, perfluorocyclopentenes, and perfluoromethylbenzenes are considered. Methods for the preparation the simplest homologs of perfluoroarenes, namely, perfluoromethylarenes with one to three trifluoromethyl groups (perfluorinated methylbenzenes, methylidiphenyls, methylnaphthalenes, methylindans, and methylpyridines) by co-pyrolysis of PTFE with perfluoroarenes have been developed. Data on co-pyrolysis of chloropentafluorobenzene with PTFE generating perfluoromethylbenzenes, chloroperfluoromethylbenzenes, and perfluoroindan are considered. Routes involving difluorocarbene and leading to perfluorocyclopentenes, perfluoromethylarenes, chloroperfluoromethylbenzenes, and perfluoroindan are discussed.

INTRODUCTION

Due to their unique properties, fluorine-containing polymers have found wide application in aerospace engineering, engineering industry, radio-electronic, electrotechnical, and chemical industries, automotive industry, medicine, and household appliances. Polytetrafluoroethylene (PTFE) is one of the major representatives of this class of polymers. Increased production and processing of this polymer, however, leads to larger amounts of waste. Investigation of thermal conversion of PTFE, therefore, is of interest from the viewpoint of seeking ways for recycling production and processing wastes.

Thermal reactions of PTFE are also interesting in that the polymer can be used as a chemical reagent to synthesize a variety of products. PTFE pyrolysis can yield tetrafluoroethylene (TFE), hexafluoropropylene, octafluoroisobutylene, or perfluorocyclobutane, which depends on pyrolysis conditions (temperature, pressure) [1]. Reduced pressure (1 torr) during pyrolysis (600 °C) increases the yield of TFE to 98 % [2], while at atmospheric pressure octafluorocyclobutane [1] is obtained. At 710–

750 °C PTFE pyrolysis gives rise to hexafluoropropylene and octafluoroisobutylene [1].

We have discovered a reaction that forms alternative products of PTFE pyrolysis. Moreover, we have also performed various co-pyrolyses using PTFE to generate trifluoromethyl groups in perfluorinated cyclopentenes and aromatic compounds. These reactions are considered in the present contribution.

EXPERIMENTAL

Pyrolyses were conducted in autoclaves made of HX18X9T steel. After experiments, the content of the autoclave was cooled to ambient temperature, taken out, and distilled with steam; then it was analyzed by GLC and NMR spectroscopy.

A liquid reaction mixture (150–170 g) was prepared from PTFE (350 g) in a 1.5 L autoclave (550 °C, 8 h). Rectification and PGLC of the mixture (350 g) gave perfluoro-1-methylcyclopentene **1** with bp 43–45 °C (25–30 mass % of the reaction mixture), small quantities (~5 %) of perfluoro-1,2-dimethylcyclopentene **2** with bp 63.4–63.7 °C, phenylhexafluorobenzene **3**

(<1 %), perfluoro-*m*- and -*p*-xylenes (<1 %), perfluorinated pseudocumene (<1 %), and mesitylene **4** (~4 %), and perfluoroparaffins (*n*-C₅F₁₂, *n*-C₆F₁₄, *n*-C₇F₁₆, *n*-C₈F₁₈) (~10–15 mass % of the reaction mixture). The structure of the compounds was verified by the data of elemental analysis, molecular weight determination, and IR and ¹⁹F NMR spectroscopy.

When PTFE was heated under similar conditions in the presence of nickel or cobalt chips (300 g of PTFE and 500 g of metal chips give 140–150 g of liquid mixture), the amount of perfluoroaromatic compounds increased five- to seven-fold and reached 25–30 % of the mass of the reaction mixture. The mixture of perfluoroaromatic compounds mostly contained mesitylene **4** and perfluoropseudocumene in a ratio of 4 : 1 to 3 : 1.

Thermal reactions of perfluorocyclopentene and -cyclohexene were conducted in a 0.1 l autoclave at 510–550 °C for 5–7 h. The reaction of perfluorocyclopentene **5** (1 g) and PTFE (1 g) at 530 °C (7 h) gave a reaction mixture (1.46 g) with 60 % compound **1**, 38 % compound **2**, and ~1 % perfluorinated xylenes and mesitylene **4**. When the quantity of PTFE was increased to 2 g and the temperature to 550 °C (5 h), the reaction mixture (1.54 g) contained 27 % compound **1**, 50 % compound **2**, and 8 % perfluoroxylenes and mesitylene **4**. Among perfluoroxylenes, *m*-isomer **6** was dominant. The reaction of perfluorocyclohexene **7** (1 g) at 530 °C (5 h) yielded a mixture of products (0.5 g) where 22 % was initial substance **7**, 65 % cyclopentene **1**, 7 % cyclopentene **2**, and 5 % perfluoromethylbenzenes, including mesitylene **4**.

Co-pyrolyses of benzene **3**, decafluorindan **8**, decafluorodiphenyl **9**, octafluoronaphthalene **10**, and pentafluoropyridine **11** with PTFE were conducted in a similar way.

Disproportionation of octafluorotoluene **12** was conducted in a 0.1 l autoclave at 550 °C (7 h). The mixture of products (66 g) obtained from compound **12** (70 g) contained (GLC data) 15 % benzene **3**, 60 % toluene **12**, 19 % perfluoroxylenes (*m* > *p*), and 2 % C₆F₃(CF₃)₃.

Pentafluorobenzene chloride **13** (60 g) reacted with PTFE (45 g) in a 0.2 l autoclave (540 °C, 2 h) to afford a reaction mixture (57–69 g) that contained 5 % initial product **13**, 8 % toluene **12**, 18 % perfluoroxylenes, 9 % mesitylene **4**,

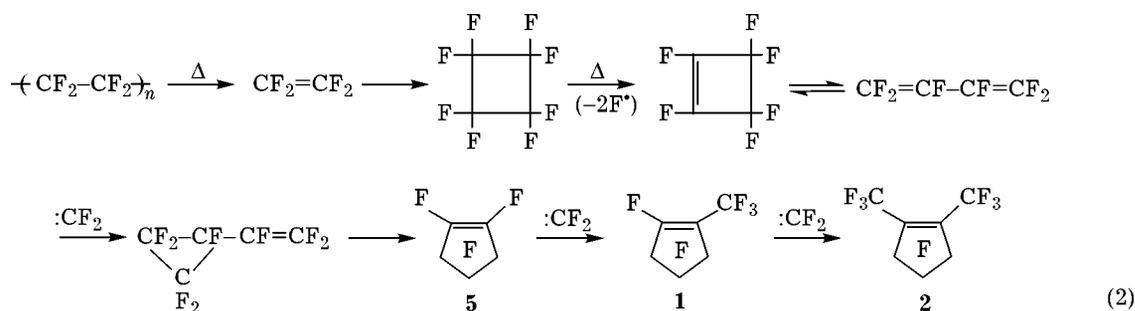
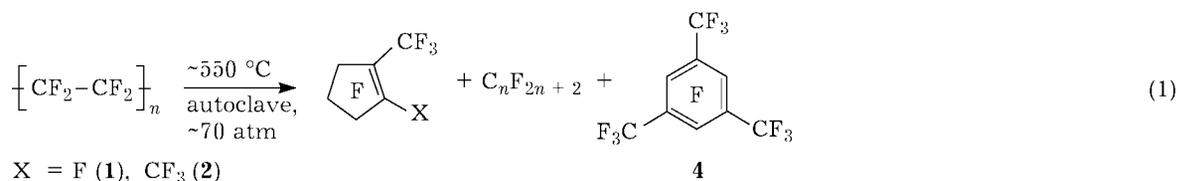
8 % heptafluorotoluene chlorides (mostly *m*-isomer), and 6 % indan **8** with admixtures of 1-chloro-3,5-bis(trifluoromethyl)trifluorobenzene and perfluoro-β-chloroethylbenzene, and 5 % perfluorotetralin mixed with tetrafluorophenyl dichlorides.

Co-pyrolyses of polyfluoroaromatic compounds with TFE were conducted in hollow quartz tubes (*l* = 650 mm, *d* = 30 mm) placed in an electric furnace. Polyfluoroarene was passed through a heated quartz tube in a flow of TFE (15 l/h). The reaction mixture was collected in a receiver cooled with an ice-salt mixture and then distilled with steam; the organic layer was separated, dried over MgSO₄, and analyzed by GLC.

From benzene **13** (51 g) and TFE (720 °C, 5 h) we obtained a mixture of products (69.6 g) that contained 47 % starting compound **13**, 12 % heptafluorobenzyl chloride **14** and *m*-chloroheptafluorotoluene **15**, 4.5 % benzene **3**, 10 % toluene **12**, and 7 % (6.6 % of theoretical) indan **8**. Rectification of 300 g of the mixture yielded individual compounds **3** (bp 80–81 °C), **12** (bp 104.5–105 °C), and **13** (bp 118.5–119.1 °C). A mixture (3 g, purity 97 % according to GLC data) of benzyl chloride **14** and toluene **15** (dominant) was isolated from the fraction rich in these compounds (bp 135.5–137 °C). In the ¹⁹F NMR spectrum of the mixture, the values of the chemical shifts and the fine structure of the signals of these products coincide with those for individual compounds **14** and **15** (according to spectral data, the ratio of **14** to **15** is ~1 : 3). Indan **8** was identified (IR and ¹⁹F NMR spectroscopy) in fractions rich in this compound.

The reaction of compound **14** (2 g) in a flow (3 l/h) of nitrogen (770 °C, 5 min) gave pyrolysate (1.3 g), which contained (GLC) 5 % benzene **3**, 13 % toluene **12**, 18 % benzene **13**, 25 % compounds **14** and **15**, 3 % indan **8**, and ~11 % *m*-dichlorotetrafluorobenzene (other isomers may also be present). The latter product and benzene **13** were also identified in the mixture by ¹⁹F NMR spectroscopy.

The reaction of compound **14** (2 g) and TFE at 770 °C (6 min) gave a mixture of products (2.1 g) that contained (GLC) 6 % benzene **3**, 12 % toluene **12**, 6 % starting compound **14**, 11 % perfluoroxylenes, ~2 % mesitylene **4**,



27 % indan **8** (it was also identified by ¹⁹F NMR spectroscopy), and ~4 % perfluorotetralin.

Conditions of co-pyrolysis of heptafluorobenzyl bromide, pentafluorophenol, and pentafluorothiophenol with TFE are found in our previous publication [3].

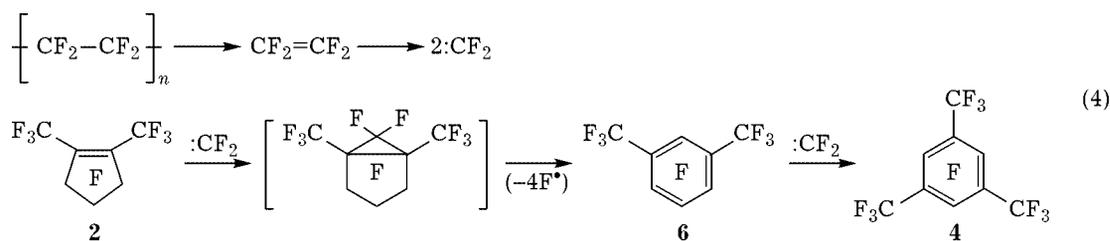
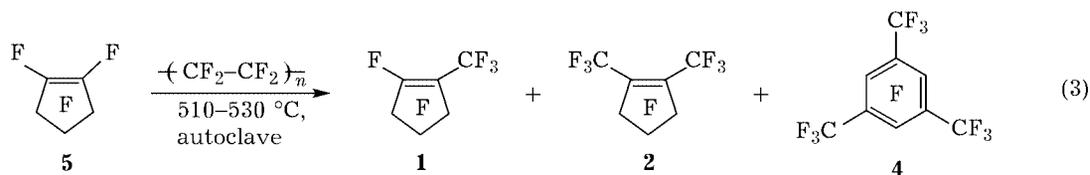
RESULTS AND DISCUSSION

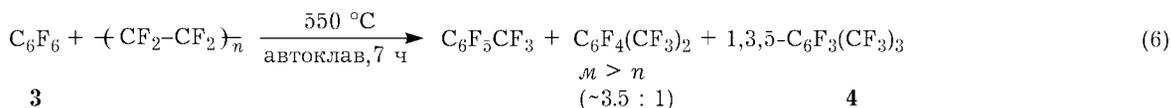
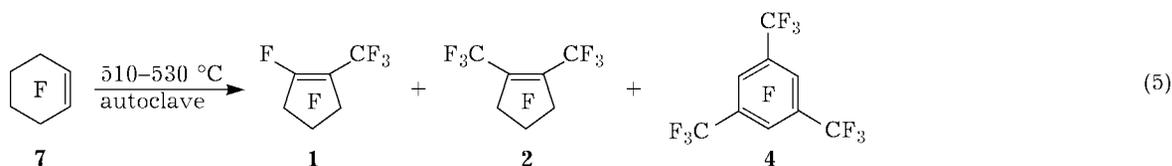
We have found that heating PTFE in an autoclave at 550 °C (8 h) yields cyclopentenes **1** and **2**, perfluoroparaffins, and perfluoroaromatic compounds. The pressure of the process increases to ~70 atm. The perfluoroparaffins found include *n*-perfluoropentane, -hexane, -heptane, and -octane, while perfluoroaromatic compounds include small quantities of benzene **3**, perfluoroxylenes, mesitylene **4** (major arene), and perfluoropseudocumene [schematic diagram (1)]. The major product of the reaction is compound **1**.

At first, PTFE apparently undergoes destruction that forms TFE dimerized into perfluorocyclobutane. Defluorination of the latter under conditions of high temperature and interaction with the autoclave wall material can give perfluorocyclobutene. Under these conditions [4], perfluorocyclobutene equilibrates with perfluorobutadiene, which is then converted to cyclopentene **5** through interaction with difluorocarbene formed during disintegration of TFE [5] (scheme (2)).

Interaction of cyclopentene **5** with difluorocarbene obviously leads to compounds **1** and **2**, as confirmed by co-pyrolysis of compound **5** and PTFE at 510–530 °C [schematic diagram (3)]. These reactions also form perfluoro-*m*-xylene **6** and mesitylene **4**. In the absence of PTFE, compound **5** practically does not change.

Formation of compounds **4** and **6** from cyclopentene **2** and :CF₂ is presented on scheme (4).





In the presence of nickel or cobalt chips, the yield of perfluoromethylbenzene products increases by a factor of 5–7. We cannot rule out potential ring expansion in cyclopentene **5** under the action of difluorocarbene (cf. [6]). However, cyclohexene **7** was not isolated from the reaction products of cyclopentene **5** with PTFE. The latter turned out to be unstable in these conditions; it converted into cyclopentenes **1** (major product) and **2** and perfluoromethylbenzenes (scheme (5)). Difluorocarbene seems to play a definite part in the given thermal conversion of **7**.

Previously, passing cyclohexene vapors **7** over an iron gauze at 550 °C led to the formation of benzene **3** [7]. However, photolysis of cyclohexene **1** formed cyclopentene **7** [8, 9].

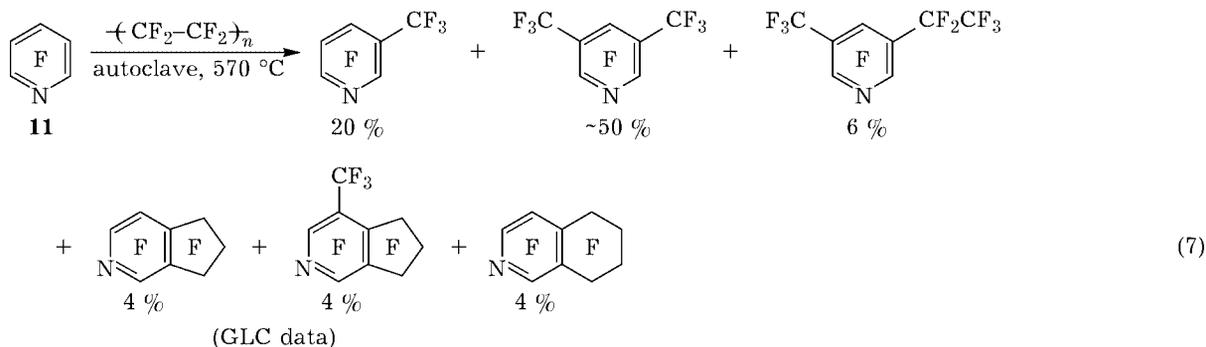
Formation of mesitylene **4** from xylene **6** under the action of difluorocarbene is in agreement with the data on co-pyrolysis of benzene **3** with PTFE (scheme (6)).

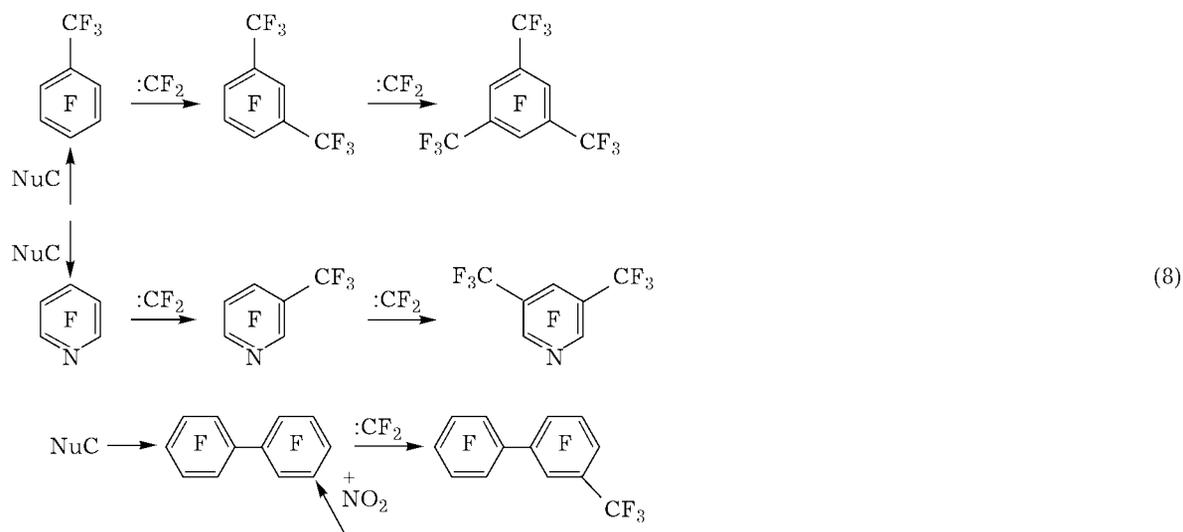
Indan **8**, diphenyl **9**, naphthalene **10**, and pyridine **11** enter similar trifluoromethylation reactions. Perfluoro-4- and perfluoro-5-methylindans (5-isomer dominates), as well as perfluoro-4,6-dimethylindan, were obtained by co-pyrolysis of PTFE with indan **8**. Perfluoro-3-

and perfluoro-4-methyldiphenyls (the former being predominant) and perfluorodimethyl diphenyls were obtained in a similar way from diphenyl **9**. Perfluorinated 2-methylnaphthalene and a mixture of 2,6- and 2,7-dimethylnaphthalenes (the latter being predominant) were obtained by trifluoromethylation of naphthalene **10** with PTFE.

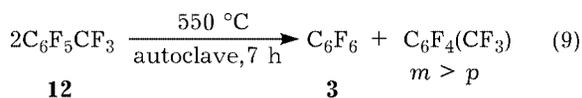
Conversion of pyridine **11** with PTFE is presented on scheme (7).

Preferable formation of *m*-trifluoromethyl-substituted products during co-pyrolysis of perfluoroarenes with PTFE may be explained by the electrophilic action of difluorocarbene [schematic diagram (8)]. In nucleophilic reactions, these compounds show a different orientation [10]. Formation of perfluoro-3-methyldiphenyl correlates with the data on orientation in the reaction of diphenyl **9** with the nitronium cation [11]. In the reaction of naphthalene **10** with :CF₂, one should expect formation of perfluoro-1-methylnaphthalene in accordance with the direction of the attack of **10** by the nitronium cation [12, 13]. However, this compound might be unstable on heating for steric reasons and might be converted into the 2-isomer. Reversibility of trifluoromethy-

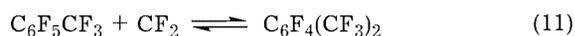
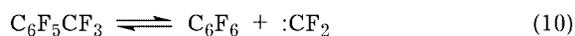




lation is demonstrated in the case of disproportionation of toluene **12** (scheme (9)).



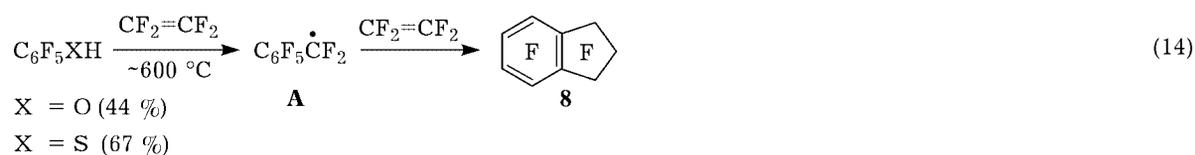
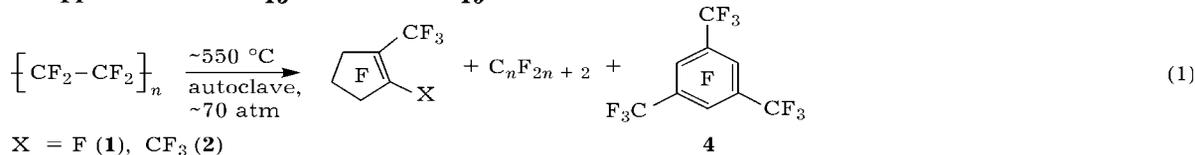
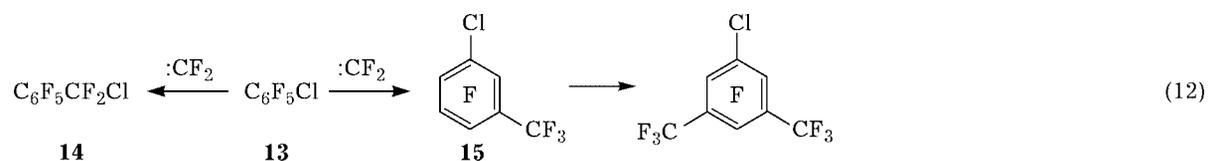
This process may be caused by disintegration of toluene **12** to benzene **3** and difluorocarbene:



Formation of trifluoromethyl derivatives could occur through difluorocarbene introduction at the $\text{C}_{\text{ar}}-\text{F}$ bond. In the case of benzene **13**, one might expect the introduction of difluorocarbene at the C-F or C-Cl bond.

Co-pyrolysis of compound **13** with PTFE gave a complex mixture of products that con-

tained toluene **12**, chloroheptafluorotoluenes, perfluoroxylens ($m > p$), mesitylene **4**, and indan **8**. No products of difluorocarbene introduction at the C-Cl bond, for example, benzyl chloride **14** have been detected during the reaction. Meanwhile, during co-pyrolysis of compound **13** with TFE, benzyl chloride **14** was detected in the vapor phase at 700°C (scheme (12)). Pyrolysis of benzyl chloride **14** (770°C) in a flow of nitrogen formed compounds **12**, **13**, toluene **15**, and indan **8**. If we assume that benzene **13** is formed during disintegration of benzyl chloride **14**, we can conclude that incorporation of difluorocarbene at the $\text{C}_{\text{ar}}-\text{Cl}$ bond in high-temperature reactions is reversible. Indan **8** may be formed by interaction of heptafluorobenzyl radical A with TFE followed by intramolecular ring forma-



tion by the radical mechanism. Indeed, co-pyrolysis of benzyl chloride **14** or heptafluorobenzyl bromide as sources of radical **A** with TFE gave indan **8** with ~80 % yield in the latter case (scheme (13)).

Hypothetically, radical **A** is involved in co-pyrolysis of pentafluorophenol and pentafluorothiophenol with TFE, giving rise to indan **8** (scheme (14)).

CONCLUSIONS

Reactions of perfluoroaromatic compounds with PTFE are of interest from the viewpoint of synthesis of perfluoroxylenes, mesitylene **4**, and perfluoro-3,5-dimethylpyridine. Using co-pyrolysis of cyclopentene **5** with PTFE is a method of preparative synthesis of cyclopentenes **1** and **2**.

Utilization of wastes after mechanical treatment of PTFE is an important practical feature of these reactions.

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