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Synthesis of perfluorinated functionalized, branched ethers

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Abstract

We wish to report synthesis of perfluorinated functionalized, branched ethers from their hydrocarbon analogues by direct fluorination. Yields up to 90%, with high purities, have been obtained at ambient temperature and pressure. This technique will likely develop into a new general method for producing perfluorinated, hyperbranched and dendritic polymers.

Keywords: Direct fluorination; Perfluorinated ethers; Hyperbranched polymers; Dendrimers

1. Introduction

Over the years, many different fluoropolymers have been synthesized. Beginning with poly(chlorotrifluoroethylene) in 1934 [1], to the accidental discovery of Teflon by Plunkett [2], many of these polymers have been found to be useful in industry. These uses include lubricants, insulators, biomaterials, coatings, and low surface tension additives [2–5].

The synthesis of these polymers typically consists of polymerization of fluorine-containing monomers. These synthesized polymers usually possess many unique thermal, chemical, and physical properties [3].

Direct fluorination, both solid and solution phase, has been used to fluorinate many types of polyethers [6–8]. Of note, is the lack of functionality outside of the ether linkages themselves present in the perfluorinated analogues. Functionalization of organofluorine compounds often involves high cost starting materials and a number of inefficiencies. Methods used for producing difunctional fluorocarbon ethers are electrochemical fluorination [9], direct fluorination [10], hexafluoropropylene oxide reactions with diacyl fluorides in the presence of alkali metal catalysts [11], and dimerization of perfluoroether acid fluorides by photolysis [12].

The area of fluorinated dendrimers is a relatively new field in fluorine chemistry. There have only been a few reported examples in the literature of synthesized fluorodendrimers [13,14]. Of these, the most common is that which has a hydrocarbon core and a fluoropolyether tail. These have been used extensively in supercritical CO_2 applications as surfactants [15]. Other dendrimers of interest were synthesized based on fluorophenylene units [16]. When synthesized, these molecules formed mesogenic liquid–crystalline phases [17]. To our knowledge, there have been no reports in the literature to date of any dendritic structures in which perfluorinated units form the core structure.

Utilizing solution-phase direct fluorination techniques, our research group has synthesized and perfluorinated branched, multi-functional compounds which are capable of being branched into novel dendritic structures. These compounds are some of the first dendritic monomers reported which are completely perfluorinated. These compounds might become useful in supercritical CO_2 applications or electronic devices.

2. Results and discussion

Using the Exfluor–Lagow fluorination process, functionalized, branched ethers have been fluorinated with high yields. Both a general scheme (Schemes 1 and 2) and a summary (Table 1) of the performed fluorination reactions are given.

A multi-functional, branched compound has been synthesized based on a pentaerythritol core (Scheme 3). This compound can have the potential use as a dendritic monomer.

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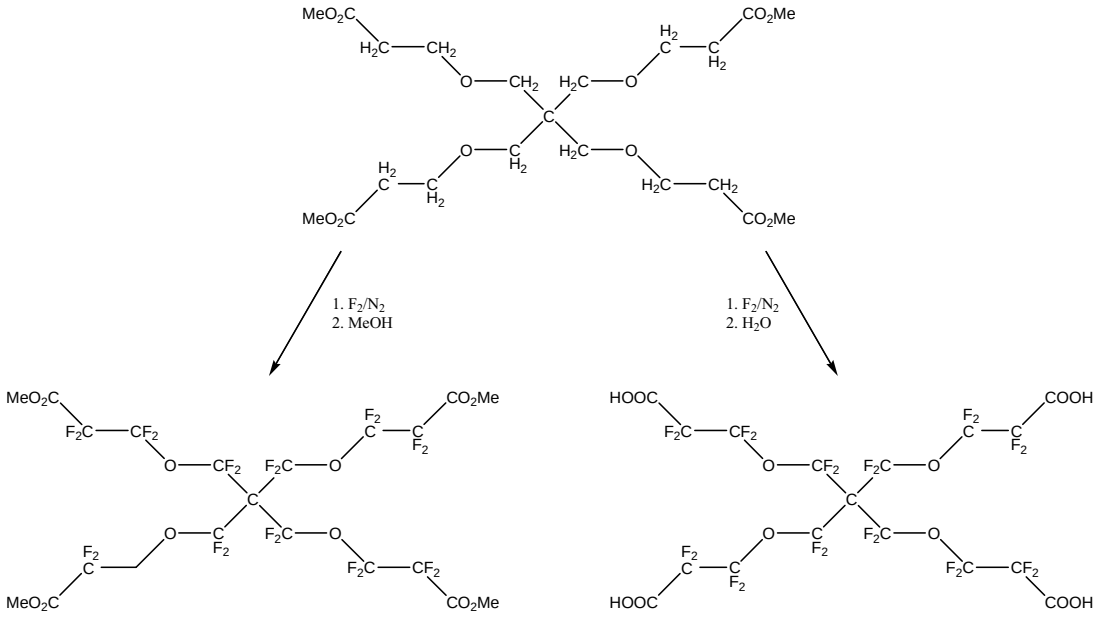
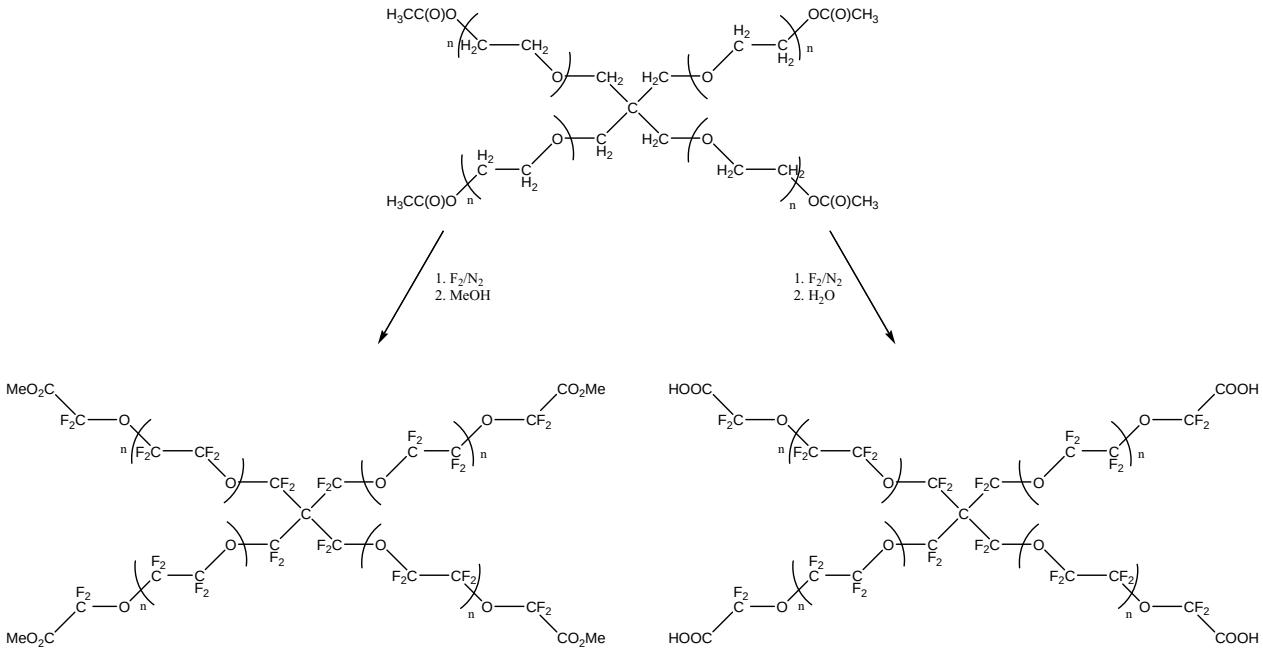


Scheme 1.



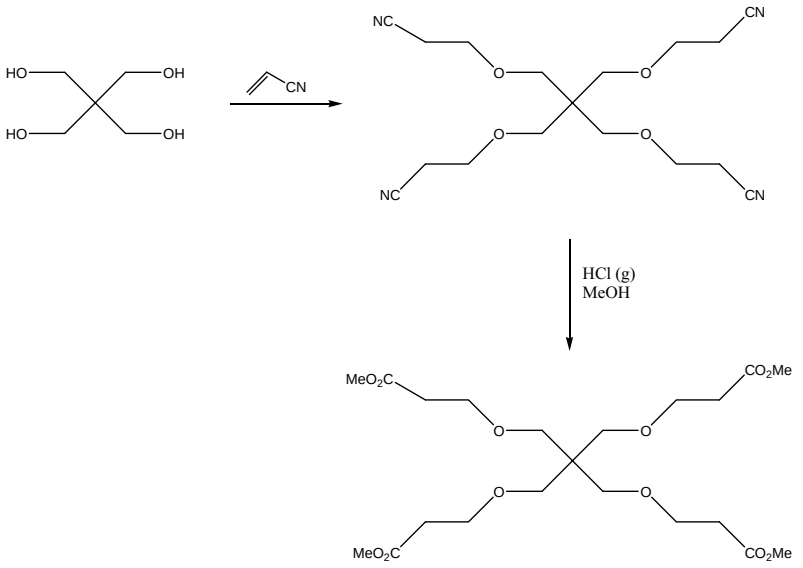
Scheme 2.

Table 1
Yields of perfluorinated functionalized, branched ethers

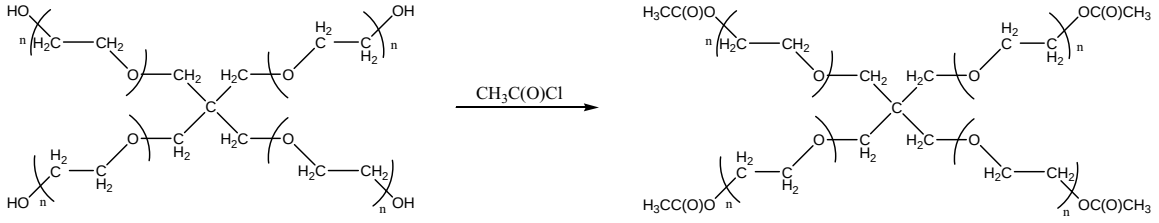
Compound	Relaxation temperature (°C)	Yield (%)
$C(CF_2OCF_2CF_2CO_2Me)_4$	RT	60.2 (isolated)
$C(CF_2OCF_2CF_2COOH)_4$	RT	40.5 (isolated)
$C[CF_2(OCF_2CF_2)nOCF_2CO_2Me]_4$	0	>90 (by mass)
$C[CF_2(OCF_2CF_2)nOCF_2COOH]_4$	0	>90 (by mass)

Pentaerythritol and acrylonitrile in dioxane/water gives a tetranitrile by a Michael addition reaction (70% yield). Esterification is achieved by refluxing in methanol under dry, acidic conditions (82% yield). For the branched polymers, pentaerythritol ethoxylate is acetylated using acetyl chloride (Scheme 4). Elemental fluorine is then passed through a solution of these materials.

The concentration of the fluorine must be initially kept low, by having a high dilution rate of N_2, to slow the



Scheme 3.



Scheme 4.

fluorination process enough to preserve the carbon–oxygen bonds. As the molecules incorporate more fluorine, more rigorous conditions are required to drive the fluorination to completion. This is achieved by increasing the fluorine concentration through dropping the rate of addition of N_2.

These reactions proceed on a very reasonable timescale. Addition of the substrate occurs over a time period of 7 h whereupon the reaction is allowed to proceed for 1 h longer. There is also no need to cool the reactor for the esters as better yields are obtained when the reactor is left at room temperature. This leads to less overall materials consumption (liquid nitrogen and elemental fluorine). A slight reduction in temperature and longer times are needed for the fluorination of the acetyl materials.

The branched compounds are perfluorinated as they are exposed to the elemental fluorine in the reactor. This includes the ester functionality. These compounds are quite stable if kept in an ambient, inert atmosphere. However, on exposure to moisture from the air, the fluoroester functionality rapidly degrades to give a perfluorinated carboxylic acid [18]. In order to quench this fluoroester functionality, methanol can be pumped into the reactor after purging. The methanol acts as a nucleophile to displace the fluoroester functionality and form a hydrocarbon methyl ester.

The functional groups can also be transformed into a variety of other moieties, such as: carboxylic acids, carboxylates, amides, chlorides, hydrides, alcohols, ethyl thioesters, cyanoethyl ethers, hydroxyethyl esters, and acid chlorides. These conversions have all been shown in detail elsewhere [3].

These tetrafunctional materials have been supplied to the research laboratories of Dr. Keith Johnston in the chemical engineering department of the University of Texas at Austin for investigation into their utility in supercritical carbon dioxide. The key to designing surfactants that can stabilize water-in-CO_2 microemulsions is to find a suitable ''CO_2-phillic'' molecular group that provides a steric barrier to aggregation. Preliminary results have shown that the difunctional linear perfluoropolyethers exhibit superior abilities to form water–CO_2 microemulsions [19,20]. The investigations into the branched materials are ongoing.

Using established organic synthetic techniques; these compounds can be branched into dendritic structures. These compounds are a few of the first reported perfluorinated core, dendritic monomers. Possible applications of these dendritic materials include uses as micelles and surfactants in supercritical CO_2. Other possible applications include uses in electronics and possibly liquid–crystalline devices.

3. Experimental

3.1. General

Pentaerythritol, acrylonitrile, pentaerythritol ethoxylate (3/4 EO/OH), and acetyl chloride were purchased from Aldrich Chemical Co. (Milwaukee, WI). Elemental fluorine was purchased from Air Products (Allentown, PA).

Low-resolution mass spectrometry was performed on a MAT TSQ-70 spectrometer. High-resolution mass spectrometry was performed on a VG analytical ZAB2-E mass spectrometer. ^{1}H and ^{13}C NMR spectra were taken on a Bruker 360 nuclear magnetic resonance spectrometer. Other ^{1}H, ^{13}C and ^{19}F NMR spectra were taken on a Varian Unity Plus-300 nuclear magnetic resonance spectrometer. ^{1}H NMR spectra were recorded at either 300 MHz or 360 MHz using C_6D_6 as the lock solvent and internal reference. ^{13}C NMR spectra were recorded at 75 and 90 MHz using C_6D_6 as the lock solvent and internal reference. ^{19}F NMR spectra were recorded at 282 MHz using C_6D_6 as the lock solvent and $CFCl_3$ as the internal reference. ^{19}F NMR chemical shifts are given in ppm with negative values denoting resonances to high field of $CFCl_3$. Direct fluorinations were performed in a similar manner to the reactions that have been previously described in the literature [21].

3.1.1. Synthesis of tetrakis-[(2-cyanoethoxy)methyl]-methane

The following synthesis was adapted from the literature [22–25]:

Pentaerythritol (12.567 g, 0.0924 mol) was dissolved in 40 ml dioxane and 2 ml water and mixed with 1 ml 40% aqueous potassium hydroxide solution. The solution was cooled to freezing in an ice bath. Acrylonitrile (36.27 g, 0.6843 mol) was added and the mixture stirred for 48 h at room temperature. The temperature was then increased to 60 °C for 8 h and allowed to cool to room temperature. Solvents were evaporated; the remaining oil was diluted in 100 ml CH_2Cl_2 and washed with 10% aqueous sodium chloride solution. The aqueous layer was re-extracted with CH_2Cl_2 and the combined organic layers were dried over sodium sulfate. Solvents were intensively evaporated by rotary evaporation and product was obtained as a white crystal, 22.543 g (0.0647 mol, 70%).

CIMS (negative mode) *m/z* (rel. int.) 349 $[M+1]^-$ (100). ^{1}H NMR (360 MHz, C_6D_6): δ 2.591 (8H, t, $J = 6$ Hz, H-3), 3.477 (8H, s, H-1), 3.651 (8H, t, $J = 6$ Hz, H-2). ^{13}C NMR (90 MHz, C_6D_6) δ 19.0 (s, C-4), 45.9 (s, C-1), 65.9 (s, C-3), 68.9 (s, C-2), 118.5 (s, C-5).

3.1.2. Synthesis of tetrakis-([2-(methoxycarbonyl)-ethoxy]methyl)methane

The following synthesis was adapted from the literature [22–25]:

Tetrakis-[(2-cyanoethoxy)methyl]-methane (9.649 g, 0.0277 mol) was dissolved in dry methanol and saturated with dry hydrogen chloride gas at room temperature. The solution was refluxed for 3 h under continuous passing of hydrogen chloride gas. During cooling, argon was passed through the setup. Hydrolysis was achieved with ice-cold water. Products were obtained through extraction with diethyl ether and drying of the organic layers over sodium sulfate. Distillation of the solvent gives the methyl ester as a light yellow oil, 10.901 g (0.0227 mol, 82%).

CIMS (negative mode) *m/z* (rel. int.) 481 $[M+1]^-$ (100). ^{1}H NMR (360 MHz, C_6D_6): δ 3.609 (12H, s, H-4), 3.565 (8H, t, $J = 6$ Hz, H-3), 3.253 (8H, s, H-1), 2.467 (8H, t, $J = 6$ Hz, H-2). ^{13}C NMR (90 MHz, C_6D_6): δ 35.0 (s, C-4), 45.4 (s, C-1), 51.8 (s, C-6), 66.6 (s, C-3), 69.6 (s, C-2), 172.5 (s, C-5).

3.1.3. Direct fluorination of tetrakis-([2-(methoxycarbonyl)-ethoxy]methyl)methane: perfluorotetrakis-([2-(methoxycarbonyl)-ethoxy]methyl)methane

The fluorination of tetrakis-[(2-cyanoethoxy)methyl]-methane was carried out in a solution phase fluorination reactor that has been described in the literature [21]. The reactor was filled with 350 ml of 1,1,2-trichlorotrifluoroethane (Freon® 113) and 30 g of NaF (0.714 mol) and kept at room temperature. The reactor was then purged with N_2 (200 cc/min) for 1 h.

Tetrakis-[(2-cyanoethoxy)methyl]-methane (2.26 g, 4.71 mmol) was dissolved in 150 ml of Freon® 113 inside a round bottom flask, and then pumped into the purged reactor at a rate of 25 ml/h. During the addition of tetrakis-[(2-cyanoethoxy)methyl]-methane to the reactor a N_2/F_2 mixture was bubbled through the reactor at a rate of 200/50 cc/min, respectively. After the solution containing tetrakis-[(2-cyanoethoxy)methyl]-methane was completely pumped into the reactor, the N_2/F_2 flow rate and the temperature was held constant for an additional hour. The flow rate was changed to 50/0 cc/min N_2/F_2, respectively, and the reactor was allowed to purge for 4 h. After the N_2 purge, 50 ml of methanol is pumped into the reactor to quench the fluoroester functionality and form the methyl ester. The solution was then filtered to remove any NaF or $NaHF_2$ and the solvent was distilled off.

Distillation of product (90 °C/100 mmHg) gave a clear, yellow liquid that was analyzed as $C(CF_2OCF_2CF_2COOCH_3)_4$ (2.83 mmol, 60.2%). CIMS (negative mode) *m/z* (rel. int.) 913 $[M+1]^-$ (100). Elemental compositions were studied by high-resolution mass spectroscopy in chemical ionization mode. Results were consistent with $C(CF_2OCF_2CF_2COOCH_3)_4$ (calculated: 913.288172; found: 913.287351). ^{19}F NMR (282 MHz, $CFCl_3$): δ −122.663 (s, 8F, –$\mathbf{CF_2}$CO–), −86.541 (s, 8F, –O$\mathbf{CF_2}$–) −76.464 (s, 8F, –$\mathbf{CF_2}$O–). ^{1}H NMR (300 MHz, C_6D_6): δ 4.089 (12H, s, H-1) ^{13}C NMR (75 MHz, C_6D_6): δ 53.453 (s, C-6), 158.544 (s, C-5).

3.1.4. Direct fluorination of tetrakis-([2-(methoxycarbonyl)-ethoxy]methyl)methane: perfluoro-3-[3-(2-carboxyethyl)-2,2-bis-(2-carboxyethoxy)methylpropxy]propionic acid

The synthesis of perfluoro-3-[3-(2-carboxyethyl-2,2-bis-(2-carboxyethoxy)methylpropxy]propionic acid proceeds as described for tetrakis-[(2-cyanoethoxy)methyl]-methane. The exception being the addition of the methanol following fluorination is omitted.

After the distillation of solvent, 10 ml of water is added to the flask to hydrolyze the compound to the corresponding acid. The product is soluble in the water layer. $C(CF_2OCF_2CF_2COOH)_4$ (1.85 mmol, 40.5%)was subsequently isolated.

CIMS (negative mode) *m/z* (rel. int.) 857 $[M+1]^-$ (100). Elemental compositions were studied by high-resolution mass spectroscopy in chemical ionization mode. Results were consistent with $C(CF_2OCF_2CF_2COOH)_4$ (calculated: 856.939779; found: 856.939056). ^{19}F NMR (282 MHz, $CFCl_3$): δ −121.111 (8F, CF_2), −85.958 (8F, CF_2), −66.549 (8F, CF_2). ^{1}H NMR (300 MHz, C_6D_6): δ 8.159 (4H, s, H-1).

3.1.5. Synthesis of tetra(ethylene glycol acetate)

Fifty milliliters of chloroform and 35.6 ml (0.5 mol) of acetyl chloride were placed in an ice cooled three-necked flask equipped with an addition funnel and a condenser under an argon atmosphere. Twenty-five grams of pentaerythritol ethoxylate (3/4 EO/OH) avg. M_n ca 270 (0.11 mol), dissolved in 40 ml of chloroform, were then slowly added to the flask with stirring. Upon completion of the addition, the flask was allowed to warm to room temperature and subsequently refluxed overnight. Excess acetyl chloride was removed under vacuum and the resulting product, $C[CH_2(OCH_2CH_2)_nOC(O)CH_3]_4$ was vacuum distilled resulting in a colorless, viscous liquid.

CIMS (positive mode) *m/z* (rel. int.) 480 $[M+1]^+$ $n=1$ (75), 656 $[M+1]^+$ $n=2$ (100). ^{1}H NMR (300 MHz, C_6D_6): δ 2.315 (3H, s, –OC(O)**CH**$_3$), 3.75 (m, –**CH**$_2$O–), 3.88 (m, –O**CH**$_2$–), 4.35 (m, –**CH**$_2$O–), 4.44 (m, –**CH**$_2$O).

3.1.6. Direct fluorination of tetra(ethylene glycol acetate): perfluoro(tetra(ethylene glycol carboxylic acid))

The fluorination of tetra(ethylene glycol acetate) was carried out in a solution phase fluorination reactor that has been described in the literature [21]. The reactor was filled with 1000 ml of 1,1,2-trichlorotrifluoroethane (Freon® 113) and 200 g of NaF (4.76 mol) and chilled to 0 °C. The reactor was then purged with N_2 (200 cc/min) for 1 h.

Tetra(ethylene glycol acetate) (4.00 g, 15 mmol) was dissolved in 350 ml of Freon® 113 inside a round bottom flask, and then pumped into the purged reactor at a rate of 25 ml/h. During the addition of tetra(ethylene glycol acetate) to the reactor a N_2/F_2 mixture was bubbled through the reactor at a rate of 400/80 cc/min, respectively. After the solution containing tetra(ethylene glycol acetate) was completely pumped into the reactor, the N_2/F_2 flow rate changed to 300/40 cc/min while the temperature was held constant for an additional hour. The ratio was then changed to 15 and 20 cc/min and the temperature was raised to 5 °C and the reaction was run for an additional 30 h. Lastly, the temperature was raised to 30 °C keeping the flow rate constant for another 14 h. The flow rate was changed to 50/0 cc/min N_2/F_2, respectively, and the reactor was allowed to purge for 4 h. The solution was then filtered to remove any NaF or $NaHF_2$. Five milliliters of water was then added to the solution and stirred overnight to hydrolyze the perfluorinated ester to the perfluorinated acid. The water was subsequently separated and distillation of product gave a clear, yellow liquid that was analyzed as the perfluoro(tetra(ethylene glycol carboxylic acids)): $C[CF_2OCF_2COOH]_4$ and $C[CF_2OCF_2CF_2OCF_2\ COOH]_4$. The yield was in excess of 90% (calculated by mass).

CIMS (negative mode) *m/z* (rel. int.) 656 $[M+1]^-$ (75), 1120 $[M+1]^-$ (100). ^{19}F NMR (282 MHz, $CFCl_3$): δ −74.6 (s, –**CF**$_2$O–), −76.6 (s, –**CF**$_2$O–), −77.5 (m, –**CF**$_2$O–), −88.5 (m, –**CF**$_2$O–).

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