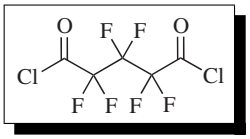
Hexafluoropentanedioyl Chloride



[678-77-3] $C_5Cl_2F_6O_2$ (MW 276.95)
InChI = 1/C5Cl2F6O2/c6-1(14)3(8,9)5(12,13)4(10,11)2(7)15
InChIKey = QOLALWJWCONGMG-UHFFFAOYAV

(used to prepare fluoroalkyl iodides or chlorides,[1–6] fluorinated heterocycles,[7,8] fluorinated ethers,[9,10] esters,[7] amides,[11] polyester,[12] polyethers[12])

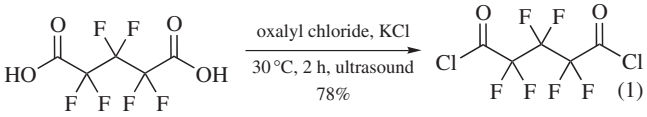
Physical Data: bp 111 °C;[1] d = 1.640 (20 °C).[13]

Solubility: soluble in ethers, alcohols, diglyme, *N*,*N*-dimethylformamide, dichloromethane.

Form Supplied in: colorless liquid; often prepared from hexafluoroglutaric acid and oxalyl chloride (or thionyl chloride).[1–3]

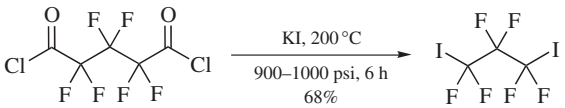
Handling, Storage, and Precautions: hexafluoropentanedioyl chloride is a corrosive compound and is sensitive to moisture; avoid storing with acids and bases; store under inert atmosphere; use in a fume hood.

Preparation of Hexafluoropentanedioyl Chloride. Hexafluoropentanedioyl chloride, sometimes called perfluoroglutaryl chloride, is commonly prepared from hexafluoroglutaric acid and oxalyl chloride (or thionyl chloride).[1–3] A typical preparation procedure is as follows:[1] the mixture of hexafluoroglutaric acid (16.7 mmol), potassium chloride (1.6 mmol), and oxalyl chloride (78 mmol) was stirred together at 30 °C for 2 h with the help of sonication, and the subsequent fractional distillation gave the hexafluoropentanedioyl chloride in 78% yield (eq 1).[1]



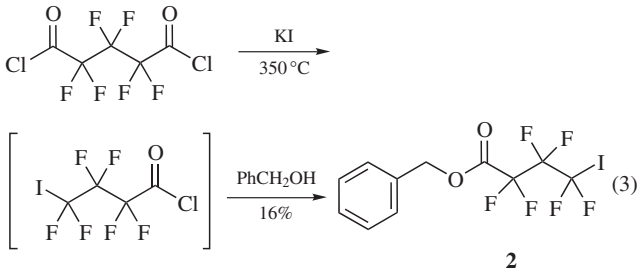
(1)

Conversion to Fluoroalkyl Iodides (or Chlorides). It has been found that hexafluoropentanedioyl chloride was readily converted to 1,3-diiodohexafluoropropane (**1**) using potassium iodide as the iodination reagent under pyrolysis conditions (eq 2).[3–5] Tournilhac and co-workers reported the formation of γ-iodohexafluorobutyryl chloride, which further reacted with benzyl alcohol to give benzyl γ-iodohexafluorobutanoate (**2**) with an overall yield of 16% (eq 3).[1,2] Compound **2** was used in the synthesis of a multiblock polyphilic liquid crystal material, which exhibited smectic A and smectic C mesophases.[2] Harris also reported that the photolysis of hexafluoropentanedioyl chloride gave 1,3-dichlorohexafluoropropane (**3**) as the major product in 71% yield (eq 4).[6]



(2)

1



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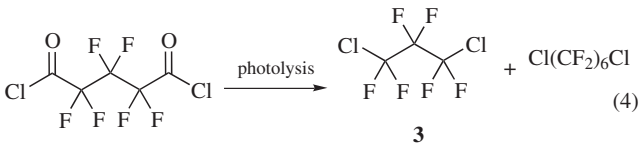
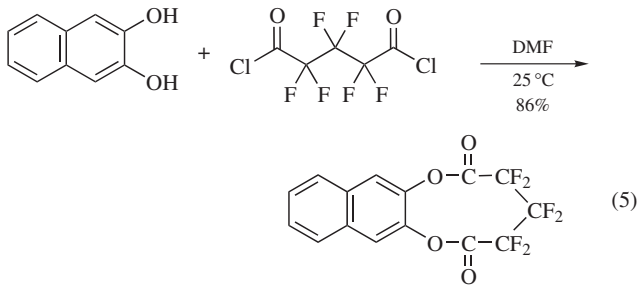


(4)

3

71% 11%

Synthesis of Heterocycles. Hexafluoropentanedioyl chloride can condense with other bifunctional compounds such as 2,3-dihydroxynaphthalene, 1,2-diaminobenzene, and *N*,*N*-bis(trimethylsilyl)piperazine to form heterocyclic compounds (eqs 5–7).[7]



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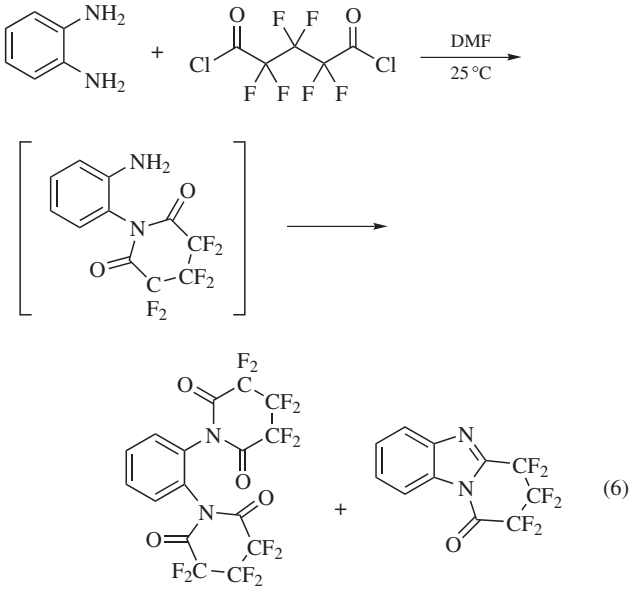
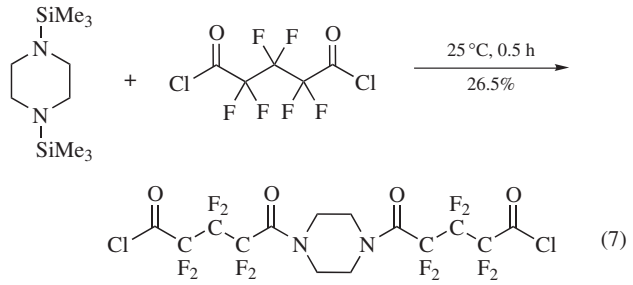


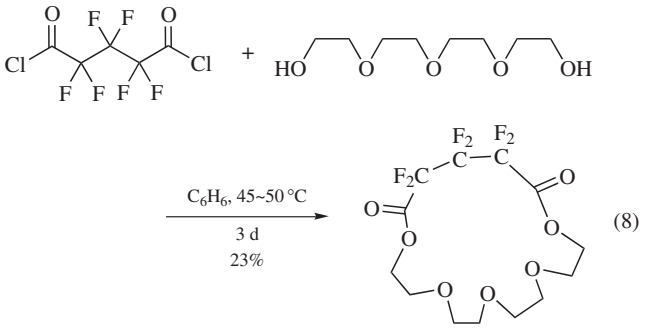
(6)

15% 21%



(7)

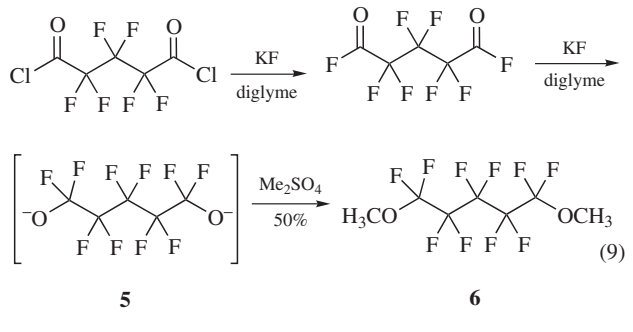
Ogunkoya reported that a macrocyclic compound 15,15,16,16,-17,17-hexafluoro-1,4,7,10,13-pentaoxacyclooctadecane-14,18-dione (**4**) could be formed in 23% yield from the condensation reaction between hexafluoropentanedioyl chloride and tetraethylene glycol (eq 8).[8]



(8)

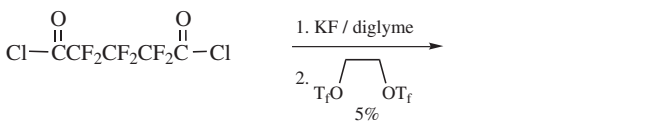
4

Synthesis of Polyfluorinated Ethers. Hexafluoropentanedioyl chloride has been used to react with an excess amount of potassium fluoride to generate perfluorinated dialkoxide (**5**) in situ. The latter can be alkylated by dimethyl sufate to give ether product **6** (eq 9).[9] When ethylene glycol bistriflate was used as the alkylating agent, polyether product **7** was produced with molecular weight Mw = 1413 (eq 10).[9] Thermally stable sodium perfluorotertiary alkoxide was also used to react with hexafluoropentanedioyl chloride to give perfluorinated ester (**8**) (eq 11).[10]



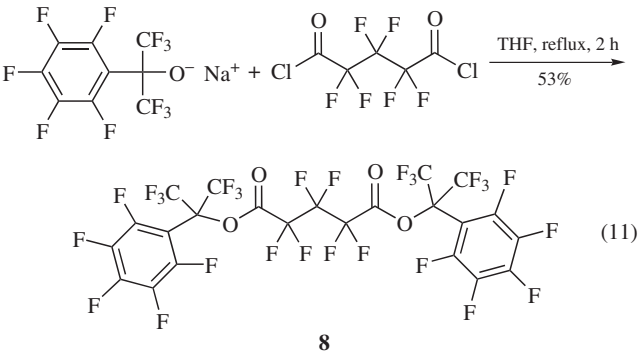
(9)

5 **6**



$$\left[\mathrm{OCF_2CF_2CF_2CF_2CF_2OCH_2CH_2}\right]_n \quad (10)$$

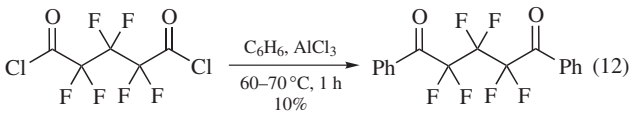
7



(11)

8

Friedel–Crafts Acylation. The Friedel-Crafts acylations of aromatic compounds with perfluorinated acyl chloride are generally difficult due to the instability of perfluorinated acyl cation species. Eapen and Tamborski reported an $AlCl_3$-catalyzed acylation reaction between hexafluoropentanedioyl chloride and benzene, and the diketone product **9** was produced in 10% yield (eq 12).[14] Similar reactions between indoles and hexafluoropentanedioyl chloride were also reported.[15]



(12)

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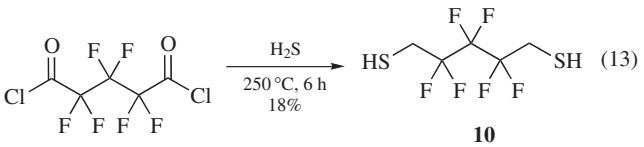
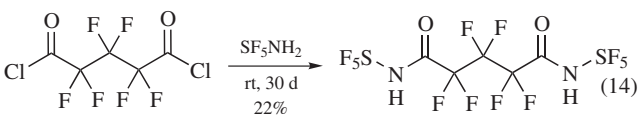
Other Reactions. Like other acyl chlorides, hexafluoropentanedioyl chloride can be readily hydrolyzed to give hexafluoropentanedioic acid.[16] The halogen-exchange reaction between hexafluoropentanedioyl chloride and sodium fluoride gives hexafluoropentanedioyl fluoride.[17] Harris and Sheppard reported that reductive thiolation of hexafluoropentanedioyl chloride with H_2S at high temperature (250 °C) afforded corresponding dithiol product **10** in 18% yield (eq 13).[18] Hexafluoropentanedioyl chloride can be also used to acylate pentafluorosulfanylamine (SF_5-NH_2) to give product **11** in 22% yield (eq 14).[11] Hexafluoropentanedioyl chloride was also used to synthesize fluorinated polyester **12** by reacting with 1,5-hexafluoropentanediol, and the polyester **12** can be further converted to polyether **13** by tranforming ester groups of the polyester to ether groups by SF_4 (eq 15).[12]



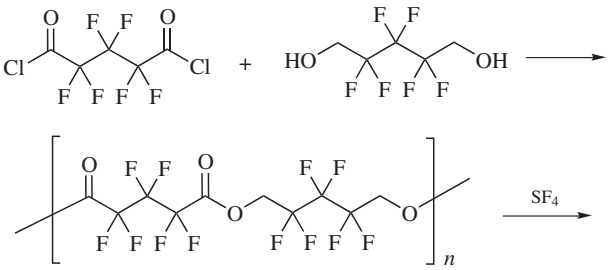
(13)

10



(14)

11



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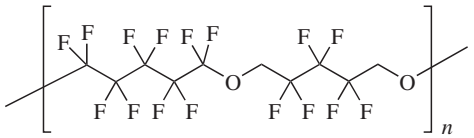

(15)

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