

4-(PERFLUOROALKYL)IODBUTANES

A. F.Gontar, V.L.Don, E.V.Igoumnova, S.M. Igoumnov

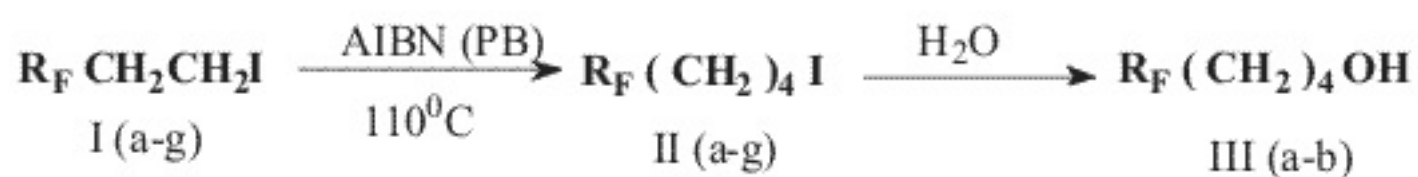
A.N.Nesmeyanov Institute of Organoelements Compounds RAS. 119991, Vavilova str.28, Moscow
e-mail: gontar@ineos.ac.ru

It has been shown earlier that perfluoroalkyliodides in the presence of radical initiators (AIBN) form both monoadducts and products of further ethylene insertion [1,2].

In this work it has been found that monoadducts (Ia-g) at a temperature of 100-110°C in the presence of ethylene are also able to react with ethylene to form corresponding 4-(perfluoroalkyl)iodobutanes (IIa-I) in 50%. See Table 1.

$\text{R}_\text{F}(\text{CH}_2)_4\text{I}$ II	BP (°C)	Conversion, %	Yield, %
CF_3 (a)	53/12 mm Hg	50	71
C_2F_5 (b)	62-64/15 mm Hg	54	63
C_3F_7 (c)	115/100mm Hg	60	58
C_3F_7 (d)	72/15 mm Hg	64	55
C_4F_9 (e)	96-97/25 mm Hg	50	75
C_6F_{13} (f)	28-30 (MP)	42	32
C_8F_{17} (g)	50-51 (MP)	40	35
cyclo- C_6F_5 (i)	93/9 mm Hg	48	38

The obtained 4-(perfluoroalkyl)iodobutanes (IIa-b) may be converted to corresponding alcohols (IIIa-b) by hydrolysis:



Experimental

5-Iodo-1,1,1-trifluoropentane (IIa)

3-Iodo-1,1,1-trifluoropropane (200g, 0.89mol) and azobisisobutyronitrile (AIBN, 3 g) are fed in a three-neck flask (1 L water capacity) equipped with a needle valve. The autoclave is pressurized, ethylene is fed to the autoclave, and the autoclave is heated to a temperature of 110°C and kept for another 4 hours. Then the excess ethylene is released through the needle valve and the liquid is discharged in a flask. 5-Iodo-1,1,1-trifluoropentane is distilled from the reaction mass at a boiling temperature of 90-95°C (80 mm Hg) and a boiling temperature of 50°C/10 mm Hg collecting fractions. 90g of the crude product is obtained. After rectification 80g of 5-iodo-1,1,1-trifluoropentane (IIa) of 97% purity remains, BP 153°C, 71% yield. (perfluoroalkyl)iodobutanes (II b-i) are obtained in a similar way (see Table 1).

5,5,5-Trifluoropentanol (IIIa)

N-Methylpyrrolidone (500mL), water(30g, 1.66 mol) and 5-iodo-1,1,1-trifluoropentane (175g, 0.89 mol) are fed in a three-neck flask (1 L water capacity) fitted with a thermometer, stirrer and backflow condenser. The reaction mixture is heated to 120°C and mixed at this temperature for 20 hours. After cooling the reaction mass to room temperature the backflow condenser is replaced for a direct one and all volatile products are distilled in vacuum of a boiling temperature of 50°C/10 mm Hg. The residue is poured into 1L of 15% hydrochloric acid. The obtained solution is extracted with ether (3X20 mL). The ether is dried over MgSO₄, ether is distilled, the residue is distilled under vacuum to yield 50g of crude product. After rectification 30g of 5,5,5-trifluoropentanol (IIIa) of 99% purity is obtained at 30 mm Hg.

5,5,6,6,6-Pentafluorohexanol (III b)

6-Iodo-1,1,1,2,2,2-pentafluorohexane (183g,0.61 mol), N-methylpyrrolidone (780 mL) and water (30g, 1.66 mol) are fed in a three-neck flask (2 L water capacity) fitted with a mechanical stirrer, thermometer and a backflow condenser. The reaction mixture is heated up to a temperature of 140-145°C and is stirred for 20 hours at this temperature. The backflow condenser is replaced by a direct one, the organic layer is separated, washed with water, dried over MgSO₄. The residue is distilled under vacuum to yield 20 g of 6-iodo-1,1,1,2,2,2-pentafluorohexane that is returned to the synthesis and 65g of 5,5,6,6,6-pentafluorohexanol (III b) of 93% purity and 35 g of 96.5% purity). The yield is 63% (taken into account conversion)

References

1. W.R. Dolbier. Chem. Rev. 1996,96,1557-1584.
2. N.O. Brace. Journal of Fluor. Chem., 93 (1999) 1-25.