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, Russia.
e-mail: ***gontar@ineos.ac.ru***

It has been shown earlier that perfluoroalkyliodides in the presence of radical initiators (AIBN) react with ethylene excess to 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^{o}C in the presence of radical initiators are also able to react with ethylene to form corresponding 4-(perfluoroalkyl)iodobutanes (IIa-I) in a 40-60% yield, conversion ca. 50%.See Table 1.

$R_F(CH_2)_4I$ II	BP (^{o}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.

$$\underset{\text{I (a-g)}}{R_F CH_2CH_2I} \xrightarrow[110^0C]{\text{AIBN (PB)}} \underset{\text{II (a-g)}}{R_F(CH_2)_4I} \xrightarrow{H_2O} \underset{\text{III (a-b)}}{R_F(CH_2)_4OH}$$

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 steel rotating autoclave (0.5L water capacity) equipped with a needle valve. The autoclave is pressurized, ethylene is fed to attain a pressure of 45 atm, the autoclave is heated to a temperature of 110^{o}C and kept for another 4 hours. Then it is cooled to room temperature, the ethylene excess is released through the needle valve and the liquid is discharged in a flask. The non-reacted 3-iodo-1,1,1-trifluoropentane is distilled from the reaction mass at a boiling temperature of 90-95^{o}C (80g), the residue is distilled under vacuum at a boiling temperature of 50^{o}C/10 mm Hg collecting fractions. 90g of the crude material is collected. After rectification 80g of 5-iodo-1,1,1-trifluoropentane (IIa) of 97% purity remains, BP 153^{o}C, 71% yield, 50% conversion. Another 4-(perfluoroalkyl)iodobutanes (II b-i) are obtained in a similar way (see Table 1).

5,5,5-Trifluoropropenpentan-1-ol (IIIa)
N-Methylpyrrolidone (500mL), water(30g, 1.66 mol) and 5-iodo-1,1,1-trifluoropentane (175g, 0.69 mol) are placed in a three-neck flask (1 L water capacity) fitted with a thermometer, stirrer and backflow condenser. The reaction mass is heated up to 120^{o}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 water-jet pump. The distillate is poured into 1L of 15% hydrochloric acid. The obtained solution is extracted with ether (3X250mL). Ether extracts are dried over $MgSO_4$, ether is distilled, the residue is distilled under vacuum to yield 50g of crude product containing 80% of 5,5,5-trifluoropentan-1-ol. After rectification 30g of 5,5,5-trifluoropentan-1-ol (IIIa) of 99% purity is produced in 30% yield , BP 73^{o}C/ 30 mm Hg.

5,5,6,6,6-Pentafluorohexan-1-ol (III b)
6-Iodo-1,1,1,2,2,2-pentafluorohexane (183g,0.61 mol), N-methylpyrrolidone (780 mL) and water (34g, 1.89mol) are placed in a three-neck flask (2 L water capacity) fitted with a mechanical stirrer, thermometer and a backflow condenser. The mixture is heated up to a temperature of 140-145^{o}C and is stirred for 20 hours at this temperature. Then the backflow condenser is replaced by a direct one, the organic layer is separated, washed with water, dried over $MgSO_4$ and distilled. There is obtained 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-pentafluorohexan-1-ol (30g 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.

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