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PRELIMINARY NOTE

# A Convenient One-Stage Synthesis of Some Diiodoperfluoroalkanes By Using Tetrafluoroethylene Derived From Poly(tetrafluoroethylene) Waste

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SUMMARY

Tetrafluoroethylene was prepared by a thermal depolymerization of poly(tetrafluoroethylene) waste. The gaseous mixture containing 95-97 % tetrafluoroethylene has been used without further purification in a direct reaction with iodine to synthesize some α,ω-diiodoperfluoroalkanes at temperature 285± 5°C for 8 h. Stoichiometric one to one ratio of the reagents has been found to produce higher diiodoperfluoroalkanes yield per unit reaction volume than synthesis in the presence of an excess of tetrafluoroethylene. This approach provides a rapid one-pot procedure to these valuable reagents without any dangerous step.

α,ω-Diiodoperfluoroalkanes with general formula $I(CF_2-CF_2)_nI$ (n= 1,2,3) are known to be useful intermediates for preparation of certain perfluorovinyl functional monomers by multi-stage synthetic procedure:

$$I(CF_2)_{2n}I \longrightarrow CF_2{=}CF{-}O{-}(CF_2)_{2n-1}COOR \qquad n=1,2,3;\ R=CH_3, C_2H_5$$

(I)

These monomers have been copolymerized with some fluoroolefins, such as tetrafluoroethylene into special fluoropolymers with excellent thermal and chemical resistance and cation-exchange properties. Thus, compound (I) (n = 2, methyl-perfluo-

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ro-5-oxa-6-hexenoate) derived from 1,4-diiodoperfluorobutane has been widely used for this purpose [1] .

Different methods for preparation of $\alpha,\omega$-diiodoperfluoroalkanes have been developed, most of these dealing with: (i) synthesis and separation of the unstable 1,2-diiodoperfluoroethane and (ii) thermal degradation or oligomerization of the latter with tetrafluoroethylene into higher products[2-5] We wish to report a convenient one stage synthesis of diiodoperfluoroalkanes by using tetrafluoroethylene 'stabilized' with small impurities derived from its preparation.

Tetrafluoroethylene (TFE) was prepared by a thermal depolymerization of poly(tetrafluoroethylene) waste Hostaflon (FRG) at 510-520°C and 5-10 mm Hg. According to GC analysis the gas contained 95-97 % tetrafluoroethylene, 2.5-4 % hexafluoropropylene and 0.5-1 % perfluorocyclobutane. The gaseous mixture was introduced without further purification into a reactor containing iodine. One stage synthetic procedure was employed, bearing in mind that 1,2-diiodoperfluoroethane is formed *in situ* at first, undergoing subsequently thermal degradation/telomerization to higher $\alpha,\omega$-diiodoperfluoroalkanes. The impurities (3-5 % hexafluoropropylene and perfluorocyclobutane) present appear to possess a 'stabilizing' effect on tetrafluoroethylene. Thus, potentially dangerous spontaneous polymerization of tetrafluoroethylene used in higher quantity within a limited reaction volume (*ca.* 200 $g.dm^{-3}$) was avoided. The reactions were carried out in stainless-steel cylinders at 285 ± 5°C for 8 h. The results were compared with those obtained in the presence of TFE excess towards iodine (Table I)

The gaseous products after reaction contained 3-4 % unreacted TFE, 50-60 % perfluorocyclobutane and 35-40 % hexafluoropropylene (experiment with TFE/$I_2$ equimolar ratio). The corresponding calculations based on the initial gaseous mixture and GLC of the products did not indicate any reaction of hexafluoropropylene. Higher than stoichiometric TFE/iodine mole ratios do not suggest any advances with respect to diiodoperfluoroalkanes yield and composition. On the contrary, the yield per unit reaction volume is diminished, whereas the amount of gaseous products increases significantly.

TABLE I

Reaction of TFE with iodine into α,ω-diiodoperfluoroalkanes

| TFE/$I_2$ mole ratio | 1 | 1,5 | 2 |
|---|---|---|---|
| Diiodoperfluoroalkanes yield | | | |
| -based on TFE-$I_2$ mixture,% | 41.4 | 31.3 | 38.9 |
| -per unit reaction volume, $g.dm^{-3}$ | 293.5 | 172.9 | 134.5 |
| Gaseous products yield based on TFE introduced,% | 7.2 | 15.1 | 24.8 |
| Diiodoperfluoroalkanes mixture composition,% (GLC) | | | |
| $C_2F_4I_2$ | 38.4 | 15.3 | 26.9 |
| $C_4F_8I_2$ | 43.7 | 39.8 | 37.1 |
| $C_6F_{12}I_2$ | 8.4 | 28.8 | 23.7 |
| $C_8F_{16}I_2$ | 2.3 | 10.4 | 8.3 |
| Unidentified (incl.higher products) | 7.2 | 5.7 | 4.0 |

Higher TFE/iodine mole ratio appears to favour a formation of more 1,6-diiodoperfluorohexane and 1,8-diiodoperfluorooctane, which are difficult to separate from the reaction mixture. Moreover, α,ω-diiodoperfluoroalkanes $I(CF_2-CF_2)_nI$ ($n \geq 3$) are of lesser practical importance with respect to preparation of perfluorovinyl functional monomers.

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