

A New Telogen for Telechelic Oligomers of Chlorotrifluoroethylene

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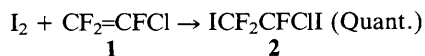
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A new telogen, $I(CF_2CFCl)_nI$ ($n = 1$) and its telomers ($n =$ average 6) are obtained by irradiation of mixtures of iodine and chlorotrifluoroethylene.

Telechelic fluorinated oligomers and polymers are of increasing importance and telechelic telogens *e.g.* ICF_2CF_2I and IC_4F_8I , derived from tetrafluoroethylene have been used extensively.¹ Chlorotrifluoroethylene **1** is an industrially significant fluorinated alkene and additions of halogens and

inter-halogens have been described²⁻⁴ but there is only one report of the addition of iodine,⁵ which indicated that a 5-30% conversion to an unstable, uncharacterised liquid occurs. We now find that a diiodide **2** can be obtained in near quantitative yield. Gamma-irradiation of a tube containing iodine and

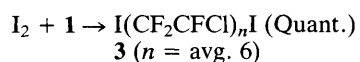
chlorotrifluoroethylene **1** gave **2** (*ca.* quantitative) as a purple liquid.



Scheme 1 Conditions: γ -rays (^{60}Co , *ca.* 1.87 Megarads), room temp.

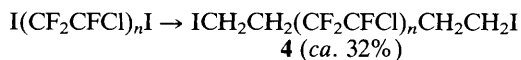
Purification of **2** was achieved by vacuum transfer but, on leaving to stand, some reversion to **1** and iodine did occur. However, this was largely eliminated by storage in the dark, with aqueous sodium metabisulphite. The structure of **2** followed from elemental analysis and mass and NMR spectrometry. The ^{19}F NMR spectrum showed an interesting ABX system, arising from the fact that fluorine atoms *Fa*, *Fb* are rendered non-equivalent by the adjacent chiral centre. ICFaFbCFxCII δ_{F} -43 (1F, dd, *Fa*), -52 (1F, dd, *Fb*), -65 (1F, dd, *Fx*).

The telogen **2** was also obtained by UV irradiation but, more importantly, telomers were also obtained, the amounts depending on conditions of the experiment. For example,



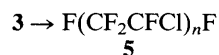
Scheme 2 Conditions: 1 kW medium pressure Hg lamp, 30 °C, 7 days irradiation of a Pyrex Carius tube containing iodine and an excess of **1**, gave a viscous liquid containing a mixture of telomers **3** where *n* averaged 6, as determined by elemental analysis and ^{19}F NMR (the ratio of the resonances corresponding to ICF_2 - and $-\text{CFCII}$ end groups, to internal groups, was determined). This telomer mixture **3** was then added to

ethylene, using platinum catalysis,⁶ and giving a telechelic cooligomer **4**. Thus, this system shows promise as a direct route to telechelic products based on chlorotrifluoroethylene.



Scheme 3 Reagents and conditions: $\text{CH}_2=\text{CH}_2$, Carius tube, 10% Pt/C, 70 °C

Direct fluorination of **3** gave **5** in high yield and provides a route to short-chain inert fluids.



Scheme 4 Reagents and conditions: F_2/N_2 (50%); $\text{CF}_2\text{ClCFCl}_2$; 10 °C

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