A New Telogen for Telechelic Oligomers of Chlorotrifluoroethylene

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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 described[2–4] 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.

$$\underset{\mathbf{1}}{I_2 + CF_2{=}CFCl} \rightarrow \underset{\mathbf{2}}{ICF_2CFClI}\ (Quant.)$$

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. ICFaFb CFxClI 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,

$$I_2 + \mathbf{1} \rightarrow \underset{\mathbf{3}\ (n = \text{avg. } 6)}{I(CF_2CFCl)_nI}\ (Quant.)$$

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 –CFClI 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.

$$I(CF_2CFCl)_nI \rightarrow \underset{\mathbf{4}\ (ca.\ 32\%)}{ICH_2CH_2(CF_2CFCl)_nCH_2CH_2I}$$

Scheme 3 *Reagents and conditions*: $CH_2{=}CH_2$, 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.

$$\mathbf{3} \rightarrow \underset{\mathbf{5}}{F(CF_2CFCl)_nF}$$

Scheme 4 *Reagents and conditions*: F_2/N_2 (50%); $CF_2ClCFCl_2$; 10 °C

Received, 28th May 1991; Com. 1/02508B

References

1 V. Tortelli and C. Tonelli, *J. Fluorine Chem.*, 1989, **43**, 199.
2 W. T. Miller, J. O. Stoffer, G. Fuller and A. C. Currie, *J. Am. Chem. Soc.*, 1964, **86**, 51.
3 D. L. Banbury, J. R. Lacher and J. D. Park, *J. Am. Chem. Soc.*, 1958, **80**, 5104.
4 R. D. Chambers, W. K. R. Musgrave and J. Savory, *J. Chem. Soc.*, 1961, 3779.
5 J. T. Barr, J. D. Gibson and R. H. Lafferty, Jr., *J. Am. Chem. Soc.*, 1951, **73**, 1352.
6 K. von Werner, *J. Fluorine Chem.*, 1985, **28**, 229.