*Journal of Fluorine Chemistry*, 9 (1977) 94–96
© Elsevier Sequoia S.A., Lausanne – Printed in the Netherlands
Received: August 26, 1976

PRELIMINARY NOTE

# The Use of Crown Ethers in the Synthesis of Hexafluoropropene and Tetrafluoroethylene Oligomers

WOJCIECH DMOWSKI,* WILLIAM T. FLOWERS, and ROBERT N. HASZELDINE

(Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD)

Fluoride ion catalyses the anionic oligomerisation of tetrafluoroethylene [1], and of hexafluoropropene [2], and since several of these oligomers are useful synthetic intermediates [1,3], methods to enable them to be prepared rapidly in good yield and high purity are now reported.

In the oligomerisation of hexafluoropropene, initiated by tertiary amines or by caesium fluoride, a mixture of the dimers,(I) and (II), and the trimers,(III), (IV), and (V) is normally obtained [2]. Use of acetonitrile as solvent enables the dimers to be obtained in good yield since they are only sparingly soluble and therefore separate from the reaction medium rather than reacting further to give the trimers. Potassium fluoride in acetonitrile provides an excellent route to dimer(I), whereas caesium fluoride in acetonitrile gives similarly good yields of dimer(II). Use of THF, in which the dimers are appreciably more soluble than the trimers, facilitates formation of the latter.

The addition of a crown ether (either 18-crown-6 or dicyclohexyl-18-crown-6 in _ca_. 0.08M conc.) to the solvent increases the solubility of the alkali metal fluoride employed [4], and has a number of beneficial effects. Thus, potassium fluoride in acetonitrile solution becomes as effective

---

*On leave of absence from the Institute of Organic Chemistry of the Polish Academy of Sciences, Warsaw, Poland.

in yielding the dimer(II) as the more expensive caesium fluoride without the crown ether. Caesium fluoride with crown ether markedly increases the rate of conversion of hexafluoropropene into the dimer(II) and trimers(III)-(V), so that the notably exothermic reaction is completed in 15 min. Use of a crown ether enables tetrahydrofuran, a solvent which is cheaper and easier to handle than dipolar aprotic solvents previously employed, to be used effectively for the preparation of the trimers in the best yields yet reported, with particular improvement in the availability of the trimer(V ). Conditions for the formation of each oligomer are summarised in the Table.

The increase in rate and yields on the addition of a crown ether is paralleled by a reduction in the formation of products [5] formed by reaction with the solvent, and hence the solvent-catalyst systems described above can be used without purification for the preparation of several batches of oligomers.

By contrast, addition of crown ether to similar solvent systems used in the oligomerisation of tetrafluoroethylene has no marked effect on the rate of reaction, yield, or distribution of the various oligomers; the limiting factor thus appears to be the concentration of the olefin in the solvent rather than the concentration of the fluoride.

1 D.P. Graham, J.Org.Chem., 31, 955 (1966); J. Hutchinson, Fette. Seifen, Anstrichm, 76, 158 (1974); R.N. Haszeldine, W.T. Flowers, W. Dmowski, G. Sparkes, and C. Vallance, EUCHEM Fluorine meeting, Monton, June 1976.

2 W. Brunskill, W.T. Flowers, R. Gregory, and R.N. Haszeldine, J.C.S. Chem.Comm., 1970, 1444; S.P. v. Halasz, F. Kluge, and T. Martini, Chem.Ber. 106, 2950 (1973).

3 W.T. Flowers, R.N. Haszeldine, C.R. Owen, and A. Thomas, J.C.S. Chem.Comm., 1974, 134; N. Ishikawa and A. Nagashima, Bull.Chem.Soc. Japan, 49, 1085 (1976).

4 C.L. Liotta and E.E. Grisdale, Tetr.Letts., 1975, 4205.

5 W. Dmowski, W.T. Flowers, and R.N. Haszeldine, in course of preparation.

TABLE

Oligomerisation of hexafluoropropene: optimum conditions for the synthesis of the individual isomers.[a]

$(CF_3)_2CF.CF{=}CF.CF_3$ (I)

$(CF_3)_2C{=}CF.CF_2.CF_3$ (II)

$(CF_3)_2C{=}C(C_2F_5).CF(CF_3)_2$ (III)

$[(CF_3)_2CF]_2C{=}CF.CF_3$ (IV)

$(CF_3)_2CF.CF{=}C(CF_3).CF_2.CF_2.CF_3$ (V)

| Predominant Oligomer (A) | Solvent (10 ml) | Catalyst | Temp ($^{o}C$) | Time (h) | Total wt. of oligomers (%)[b] | Wt. of dimer fraction (%)[b] | Wt. of trimer fraction (%)[b] | % of (A) in appropriate fraction |
|---|---|---|---|---|---|---|---|---|
| (I) | $CH_3CN$ | KF (1 g) | 20 | 20 | 92 | 92 | 0 | 94[c] |
| (II) | $CH_3CN$ | CsF (0.5 g) | 20 | 20 | 92 | 92 | 0 | 100 |
| (II) | $CH_3CN$/CE | KF (1 g) | 20 | 18 | 96 | 89 | 7 | 100 |
| (III) + (IV) | THF/CE | CsF (0.5 g) | 20 | 0.25 | 95 | 37 | 58 | 98[d] |
| (III) + (IV) | THF/CE[e] | CsF (0.5 g) | 20 | 2 | 100 | 6 | 94 | 98[d] |
| (V) | THF/CE | CsF (0.5 g) | 130-200 | 5 | 94 | 34 | 60 | 100 |

[a] Reactions were carried out with shaking in sealed 80 ml tubes loaded with 6 g hexafluoropropene.

[b] Yields throughout are based on wt. % of hexafluoropropene loaded.

[c] Contained 6% of (II).

[d] Contained 2% of (V).

[e] In this reaction hexafluoropropene was added as the reaction proceeded and at such a rate as