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PRELIMINARY NOTE

Copper-Induced Telomerization of Tetrafluoroethylene with Fluoroalkyl Iodides

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SUMMARY

In the presence of catalytic amounts of copper, telomerization of tetrafluoroethylene with fluoroalkyl iodides can be carried out at 80~100°C. As compared with usual high-temperature (~200°C) telomerization process, the reaction time required is much shorter.

All the commercial organofluorine surfactants and textile chemicals contain a C6-C12 fluorocarbon segment. Currently, the fluorocarbon intermediates required are prepared either by electrochemical fluorination or from tetrafluoroethylene[1]. The latter route is through telomerization of tetrafluoroethylene with fluoroalkyl iodides, which was first reported by Haszeldine thirty-seven years ago[2]. Although many modifications have been made to this process, the elevated temperature necessitated (~200°C) and the wide spread of telomers $R_f(CF_2CF_2)_nI$ remain the main disadvantages. In order to lower the telomerization temperature there have appeared several patents using organic peroxides as initiators[3]. In connection with our previous work describing that copper could induce the addition reaction of fluoroalkyl iodides to alkenes under mild conditions via single electron

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transfer (SET) mechanism[4], we envisioned that if tetrafluoroethylene instead of non-fluorinated olefin was used in the reaction the telomerization conditions and product distribution might be improved.

It was found that in the presence of catalytic amounts of copper the telomerization of tetrafluoroethylene proceeded smoothly when perfluoroethyl iodide(1), ω-chloroperfluorobutyl iodide(2) and 5-fluorosulfonyl-3-oxo-perfluoropentyl iodide (3) were used as telogens. The representative results are listed in Tables I,II and III. High temperature telomerizations of the same reactants were also carried out and are shown in the Tables for purpose of comparison, although they had previously been reported in literature (for 1 [6], 2 [7] and 3 [8]).

The first distinct point,as shown in Tables I-III is that the telomerization temperature in these reactions was lower(80-100°C). The lower temperature and consequently lower autogenous pressure provide more convenient and safe conditions in operations. The second feature to notice about these reactions is that the time required to complete the reaction was significantly shorter (Entry 8) as compared with that for the usually corresponding high temperature telomerization (Entry 10), see Table IV.

Concerning the product distribution, as is well known, the choice of the reactant ratio is the main control for the value of n in the telomer. Four ratios of reactants of each fluoroalkyl iodide with tetrafluoroethylene have been used and the results are shown in Tables I-III. The telomer distribution was different among these telogens even when in a similar reactant ratio. This was to be expected because they have different chain-transfer constants, although all of them are "primary" fluorocarbons[9]. In spite of the variation of reactant ratios a larger range of telomers was produced using all the telogens. The undesired solid products (i.e.>C10) increased with lowering the reactant ratio (R_fI/C_2F_4). However, as compared with the high temperature telomerization the yields of C6-C10 were better. Furthermore, in the copper-induced telomerization no perfluorocyclobutane was produced.This is an unavoidable product in the high temperature reaction.

TABLE I

Telomerization of $CF_2=CF_2(\underline{4})$ with $CF_3CF_2I(\underline{1})$[a]

Entry	$\underline{1}$ g(mol)	C_2F_4 g(mol)	$\underline{1}$:$\underline{4}$	T (°C)	P(max) Kg/cm2	t (min)	Products, $F(CF_2)_nI$, g(mol%[b]) n=2	n=4	n=6	n=8	n=10	n>10[c]
1	25.5 (0.104)	5.2 (0.052)	1:0.5	90- 100	20.6	300	11.1	1.9 (10.5)	2.0 (17.2)	1.5 (15.9)	0.2 (2.4)	8.3
2	19.4 (0.079)	7.9 (0.079)	1:1	100	28.3	300	7.5	1.8 (6.6)	1.3 (7.4)	1.1 (7.6)	0.1 (7.8)	7.3
3	16.9 (0.069)	10.3 (0.10)	1:1.5	100	30.5	450	5.6	2.0 (5.6)	1.2 (5.2)	1.3 (6.9)	1.8 (6.2)	14.5
4	14.0 (0.057)	11.4 (0.11)	1:2	100	33.5	480	3.8	1.2 (3.0)	1.3 (5.1)	0.3 (1.4)		18.4
5[d]	9.8 (0.04)	6.0 (0.06)	1:1.5	180- 190	32.0	740	5.1	0.2 (1.0)	0.6 (4.5)	0.2 (1.8)	2.2[e] (36.7)	5.0

[a] 2 g of copper was used unless noted otherwise; [b] the composition was determined by ^{19}F NMR and GC. Yields are based on tetrafluoroethylene (mol%)[5] unless specially noted; [c] solid product expressed in grams; [d] no copper was added; [e] perfluorocyclobutane.

TABLE II

Telomerization of $CF_2=CF_2(\underline{4})$ with $Cl(CF_2)_4I(\underline{2})^a$

Entry	$\underline{2}$ g(mol)	$\underline{4}$ g(mol)	$\underline{2}:\underline{4}$	T (°C)	Pmax Kg/cm2	t (min)	Products, $Cl(CF_2)_n$, g(mol%^{b})				
							n=4	n=6	n=8	n=10	n>10^c
6	54.4 (0.15)	3.74 (0.036)	4:1	80- 90	7.1	60	34.2	5.7 (32.9)	3.2 (30.4)	0.5 (6.0)	1.7
7	54.4 (0.15)	7.5 (0.075)	2:1	80- 90	17.5	60	25.1	11.6 (33.4)	3.2 (15.2)	7.1 (42.9)	8.0
8	54.4 (0.15)	12.0 (0.12)	2:1.6	80- 90	22.0	60	13.9	13.9 (25.0)	20.5 (60.7)	0.2 (0.75)	3.7
9	54.4 (0.15)	15.0 (0.15)	1:1	80- 90	24.4	60	19.5	11.4 (16.4)	8.2 (19.4)	1.5 (4.5)	22.2
10^d	40.0 (0.11)	8.3 (0.083)	2:1.5	180	25.0	300	18.9	11.43 (29.4)	5.4 (23.1)	0.3^e (3.6)	2.6

a,b,c,d and e as noted in Table I.

TABLE III

Telomerization of C_2F_4(4) with $I(CF_2)_2OCF_2CF_2SO_2F$(3)[a]

Entry	3 g(mol)	C_2F_4 g(mol)	3:4	T (°C)	P(max) Kg/cm2	t (min)	Products, $I(CF_2)_nO(CF_2)_2SO_2F$, g(mol%[b]) n=2	n=4	n=6	n=8	n=10	n>10[c]
11	63.9 (0.15)	3.75 (0.038)	4:1	90	10.5	180	52.8	2.0 (10)	1.7 (14.5)	1.2 (13.2)	0.3 (3.8)	0.4
12	60.0 (0.14)	7.0 (0.07)	2:1	90	14.6	180	37.9	6.5 (17.7)	3.8 (17.4)	1.9 (11.2)	0.4 (2.8)	8.8
13	60.0 (0.14)	10.5 (0.11)	2:1.5	90	23.3	210	25.4	13.0 (23.5)	6.8 (20.7)	3.1 (12.2)	0.7 (3.2)	15
14	60.0 (0.14)	14.0 (0.14)	1:1	90- 100	22.6	180	29.2	11.4 (15.5)	5.0 (11.4)	1.4 (4.1)	0.1 (0.4)	21.3
15[d]	42.6 (0.1)	7.5 (0.075)	2:1.5	180- 190	26.0	480	17.1	12.0 (30.4)	3.4 (14.5)	0.6 (3.3)	3.1[e] (41.3)	1.7

a.b.c.d and e as noted in Table I.

TABLE IV

Time consumed to complete the telomerization of C_2F_4 with 2

Entry 8			Entry 10		
t(min)	T(°C)	P(kg/cm2)	t(min)	T(°C)	P(kg/cm2)
30	68	20.6	30	110	17.9
35	80	22.0	65	160	23.5
40	82	21.5	85	168	25.0
45	83	20.0	100	170	25.5
50	85	15.0	120	170	23.0
55	88	9.3	140	180	22.0
60	91	5.9	160	185	20.5
80	96	0.8	180	170	18.0
85	98	0.1	200	185	19.0
90	98	<0.1	...	...	....

Similarly, $Pd(PPh_3)_4$ could also induce the telomerization of tetrafluoroethylene with fluoroalkyl iodides.

In conclusion, all above data show that the copper induced telomerization of tetrafluoroethylene with fluoroalkyl iodides can be carried out fast under mild conditions giving the corresponding telomers with somewhat better desired composition as compared with the high temperature reaction. In order to keep the value of n within the preferred range a step-wise addition of tetrafluoroethylene to excess fluoroalkyl iodides can be taken[8,10]. For this purpose the lower reaction temperature, pressure and short time required, apparently, are favorable.

EXPERIMENTAL

Typical telomerization procedure: An autoclave (100 ml) was charged with freshly prepared copper powder (2g). A required quantity of fluoroalkyl iodide and tetrafluoroethylene was added by vacuum transfer. The autoclave was rocked at 80-100°C for several hours until the pressure did not drop further. Recovered iodide and/or olefin were collected by venting through a trap cooled in liquid air and then a violet liquid was obtained from autoclave.Distillation gave the fractions.The composition of crude product was determined by ^{19}F NMR and GC(as shown in Tables I-III).

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