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HOMOLYTIC ADDITION OF FUNCTIONALLY SUBSTITUTED PERFLUOROALKYL IODIDES

L. N. Kiseleva, V. I. Dostovalova, F. K. Velichko, V. F. Cherstkov, S. R. Sterlin, G. I. Savicheva M. A. Kurykin, and L. C. German

Unlike well-investigated reactions of perfluoroalkyl iodides with unsaturated compounds [1], functionally substituted perfluoroalkyl iodides (FP's) under radical conditions have been little studied. Telomerization of vinyl chloride with  $FSO_2CF_2I$  was studied [2], and there are data on addition of  $I(CF_2)_nO(CF_2)_2SO_2F$  (n = 2-4) to double bonds initiated by benzoyl peroxide (BP) [3] and in the presence of sodium hydrosulphite ( $Na_2S_2O_4$ ) [4]. Reactions of FP's with unsaturated compounds are of great interest since they can serve as a method for obtaining derivatives of iodofluorohydrocarbons containing functional groups.

We have investigated the capacity of a number of FP's to attach to 1-hexene and methyl acrylate under thermal, peroxide (di-tert-butyl peroxide, TBP), and metallocomplex initia-tion[FE(CO), + DMF]. At equimolar reagent ratios all three types of initiation direct the reaction toward adduct formation by the scheme

$$\begin{split} R_FI &+ CH_2 = CHC_4H_9 \rightarrow R_FCH_2CHIC_4H_9 \\ (Ia-g) & (IIa-g) \\ R_FI &+ CH_2 = CHCOOMe \rightarrow R_FCH_2CHICOOMe \\ & (Ia,b) & (IIIa,b) \\ R_F &= (CF_3)_2CFCF = CFCF_2 (a), \ NCCF_2 (b), \ H_3COOCCF_2 (c), \ CF_3CF_2CF_2 (d), \\ CF_3(CF_2)_4CF_2 (e), \ FO_2SOCF_2CF_2 (f), \ (CF_3)_2CFOCF_2CF_2 (g). \end{split}$$

Under thermal initiation, in which the susceptability of the FP C-I bond to thermal homolysis is the main factor, the investigated compounds fall into the following series of decreasing adduct yield upon reaction with 1-hexene:  $(CF_3)_2CFCF=CFCF_2I$  (Ia)  $\geq NCCF_2I$  (Ib) >  $H_3COOCCF_2I$  (Ic) >  $CF_3CF_2CF_2I$  (Id)  $\geq CF_3(CF_2)_4CF_2I$  (Ie) >  $FO_2SOCF_2CF_2I$  (If) >  $(CF_3)_2CFOCF_2-CF_2I$  (Ig).

As seen from Table 1, upon thermal initiation FP's (Ia-c) attack 1-hexene significantly easier than iodides without functional substituents (Id, e). This is obviously associated with certain structural features: the allyl position of the iodine atom in (Ia) and the presence of an electron-accepting substituent in the  $\alpha$ -position to the reaction center in (Ib, c). One notes the comparatively low capacity of FP's (If, g) which have an OR substituent  $\{R = SO_2F, CF(CF_3)_2\}$  in a  $\beta$ -position to the iodine atom to form adducts with 1-hexene under thermal conditions.

Upon initiation of the reaction with TBP under chosen conditions the differences in the capacity of iodides (Ia-g) to attach to 1-hexene diminish and all adducts are formed with yield of 70-98%.

In the case of iodofluorosulfate (If) the expected increase of adduct yield is observed upon going from thermal to peroxide initiation (Table 1), while initiation with  $Fe(CO)_5 + DMF$  is not very effective. It was shown in a separate experiment (see experimental part) that  $Fe(CO)_5$  reacts with (If), forming  $IFeOSO_2F$ , in consequence of which the  $Fe(CO)_5$  concentration in the reaction mixture decreases, lowering the initiation efficiency. For the most inert compounds under thermolysis conditions the  $Fe(CO)_5$ -DMF system(Ig) gave better results than thermal and peroxide initiation (experiment 7).

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2132-2138, September, 1988. Original article submitted April 1, 1987. TABLE 1. Addition of Perfluoroorganic Iodides (4 mmoles) to Unsaturated Compounds (4 mmoles) (140°C, 2 h, 1 atm of  $N_2$ ) under Conditions of Thermal, Peroxide (TBP)<sup>\*</sup>, and Metallocomplex {Fe(CO), + DMF)<sup>†</sup>} Initiation

Addend			Adduct yield, %				
		4.4.4	Addend conversion %				
		Adduct	thermolysis	TBP	Fe(CO)s+ DMF		
			Monomer-1-he	kene			
	(Ia)	(IIa)	83	98	81		
	(Ib)	(IIb)	80	95	52		
	(Ic)	(IIc)	45	80	70		
	(I <sub>'d</sub> )	(IId)	$\frac{-35}{-24}$	95	<u>92</u>		
ġ	(I <u>e</u> )	(IIe)	$\frac{20}{20}$	90	100 <u>95</u>		
	(If)	(IIf)	$\frac{10}{10}$	90			
	(Ig)	(IIg)	$\begin{array}{c} 13 \\ 3 \\ \hline 6 \end{array}$	$\frac{95}{70}$	<u> </u>		
		M	lonomer-methaci	rylate			
	(Ia)	(IIIa)	78	Resinifica-	96		
	(I,b)	(IIIb)	$\frac{50}{58}$	$\frac{30}{49}$	$ \begin{array}{r} 100 \\ -40 \\ -49 \end{array} $		

\*10 mole % of TBP per unsaturated compound. \*10 mole % of Fe(CO)<sub>5</sub> and 30 mole % of DMF per unsaturated compound.

TABLE 2. Competing Addition of Perfluoroorganic Iodides (Ia, d, g) (4 mmoles) to 1-Hexene (4 mmoles) (140°C, 2 h, 1 atm of  $N_2$ ) under Conditions of Thermal and Peroxide Initiation

	Relative yield of adducts, %					
Addends	Thermolysis	TBP*				
$(I_a) + (I_d)$ $(I_a) + (I_g)$ $(I_d) + (I_g)$	95(IIa)+5(IId) 98(IIa)+2(IIg) 70(IId)+30(IIg)	87 (IIa) +13 (IId) 95 (IIa) +5 (IIg) 60 (IIc) +40 (IIg)				

\*10 mole % per 1-hexene.

The investigated addends fall in the following series by their relative capacity to attach to 1-hexene in competing reactions under thermal and peroxide initiation (Table 2): (Ia) > (Id) > (Ig).

In reaction with methyl acrylate (Table 1) under selected conditions only compounds (Ia, b) form adducts (in the remaining cases monomer polymerization occurs) and the  $Fe(CO)_5$ -DMF system with (Ia) (trans-isomer [5]) yields adduct (IIIa) in 96% yield, while peroxide initiation leads to resinification of the reaction mixture. The high yield of adduct (IIIa) under thermolysis conditions indicates that resinification with TBP initiation is not associated with the reaction conditions (temperature or duration) but with secondary reactions of tert-butoxyl radicals with monomer. The negative result obtained in the reaction of (Ic-g) with methyl acrylate agrees with the positions of these iodides in the series of addition capacity to the double bond of 1-hexene with thermal initiation. Owing to the relatively high stability of the C-I bond in these compounds, chain transfer is obviously impeded and polymerization of the monomer takes place.

99	$\delta^{-13}C, ppm$ of the C ato	from TMS m)	(in brac	ckets:	atom number	Coupling constant, Hz <sup>1J</sup> C-F
.Compound*		13CF3	<sup>18</sup> CH, CF2	IHDet	Х, Ү	$iJ_{C-C-F}$ : $[J_{C-H}]$
(CFa) <sub>3</sub> CFCF=CFCF <sub>2</sub> I (Ia)	119,1, 87,8, 135,5, 149,7	81,9	1	I	I	$\left[\frac{288}{26}(1), \frac{265}{27; 37}(3), \frac{265}{29; 37}(4), \frac{314}{35}(5)\right]$
(GF <sub>3</sub> ) <sub>2</sub> CFCF=CFCF <sub>2</sub> CH <sub>2</sub> CHICH <sub>2</sub> C <sub>3</sub> II <sub>7</sub> (IIa)	120,4, 87,9, 140,9, 150,3	117,8	47,0	21,0	41.0, 32.5, 22.3, 14.0(8-11)	$\frac{288}{26}(1), \ \frac{263}{26; \ 36}(3), \ \frac{264}{34cp}(4), \ \frac{249}{31}(5),$
						$\frac{1}{24}(6)$
(CF <sub>3</sub> ) <sub>2</sub> CFCF=CFCF <sub>2</sub> CH <sub>2</sub> CHICOOCH <sub>3</sub> (IIIa)	118,8, 87,9, 139,7, 148,6	115,9	41,5	4,3	170,1, 52,1 (8-9)	$\frac{290}{26}(1), \frac{-}{24}(6)$
CF3CF2CF2[ (Id)	115,1, 106,2	91,3	I	ł	1	$\frac{288}{34} (1), \frac{283}{35} (2), \frac{318}{41} (3)$
CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> CH <sub>2</sub> CH1CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>5</sub> (IId)	117,6, 107,3	117,1	42,4	20,2	$\begin{array}{c} 40.7, \ 32.3, \ 22.2, \\ 14,0(6-9) \end{array}$	$\frac{287}{34}(1), \frac{264}{37}(2), \frac{257}{31}(3), \frac{-}{21}(4)$
CF3CF2CF2CF2CF2I (Ie) †	118,5,109-112(2-5)	94,4	1	I	ł	$\frac{287}{33}$ (1), $\frac{321}{42}$ (6)
CF3CF2CF2CF2CF2CF2CF2CH2CHICH2C3H7 (IIe)	118,2,109-112(2-5)	118,9 (6)	42,9	20,5	41,0, 32,6, 22,4, 14,0(9-12)	$\left[\frac{288}{33}(1), \frac{258}{34}(6), \frac{1132}{21}(7), \frac{1152}{-}(8)\right]$
(CF <sub>3</sub> ) <sub>z</sub> CFOCF <sub>z</sub> CF <sub>z</sub> I (Ig)	117.0, 101,2, 113,8(3)	88,1	)	 	}	$\left \frac{287}{31}(1), \frac{267}{39}(2), \frac{289}{32}(3), \frac{319}{42}(4)\right $

TABLE 3. <sup>13</sup>C NMR Chemical Shifts and Coupling Constants in Compounds (I) and X-R<sub>F</sub>CF,CH,CHI-Y (II), (III)

$- \begin{array}{ c c c c c c c c c c c c c c c c c c c$

\*Carbon atoms in compounds are numerated from left to right. Agrees with results of [8] obtained with broad-band attenuation of the C-F coupling.

Adduct	Bp, °C(p, mm Hg)	n <sup>20</sup> nD	d.,20	Molecular formula	Found Calculated		
					с	н	F
(IIa)	55(2)	1,3960	1.6666	C12H12IF11	29.38	2,47	42,36
(IIIa)	90(12)	1,3915	1,7684	C10H8IF11O2	29,29 24,78	2,46 1.31	42,47 42,28
(lIb)	56(5)	1,4620	1,1896	C8H12IF2N	24,31 32.79	1,23 4,22	42,30 12,87
(IIIb)	72(5)	1,4052	1,3416	C6H6IF2NO2	33,47 24,75	4,21 2,14	13,24 13,02
(IIc)	60(2)	1,4600	1,3112	C <sub>9</sub> H <sub>15</sub> IF <sub>2</sub> O <sub>2</sub>	24,93 33,49	2,09 4,90	13,15 11,48
(114)	55(10)	1.4040	1.3826	CoH 191F7	33,76 28,36	4,72 3,26	11,87 35,08
(IIG)	77 (5)	1 3820	1 5026	CurturiFu	28,44	3,18 2,34	34,99 46 62
(116)	79(9)	4 4260	1,8004	C.H. IF.O.S	27,19	2,28	46,59
(111)	12(2)	1,4200	1,0004	C811121F3O35	23,41	2,95	23,16
(IIg)	63(5)	1,3772	1,6882	U11H12IF110	26,40	$\frac{2,51}{2,42}$	$\frac{42,14}{42,12}$

TABLE 4. Characteristics of Adducts (II) and (III)

The composition of adducts (II) and (III) was confirmed by elemental analysis and their structures were proved by <sup>13</sup>C NMR. For comparison, spectra of the starting perfluoroorganic iodides (Ia-g) were obtained (Table 3). In the spectra of compounds (I) the signals of the  $CF_2I$  end group { ${}^{1}J_{C-F}$  = 320 Hz,  $\delta$   ${}^{13}C$  81-93 ppm, with the exception of 63.1 ppm for nitrile (Ib)} are characteristic. In the adducts of (Ia-g) to 1-hexene or methyl acrylate a characteristic CHI signal appears in the region of ~20 and 4 ppm for esters (IIIa, b) (Table 3), and the  $CF_2X$  (X = alkyl, substituted alkyl) signal moves downfield (118-115 and ~110 ppm for nitriles). These data agree only in their order with the previously observed regularity of the influence of the iodine  $\alpha$ -atom on  $\delta$  <sup>13</sup>C<sub> $\alpha$ </sub> [6]. It should be noted that  $\delta$  <sup>13</sup>C of CHIAlk is ~6 ppm lower than the value obtained by [6] with calculation of the  $\gamma$ -effect of two fluorine atoms ( $\gamma_F = -6.8$  ppm [7]). This indicates a significant contribution to the  $\delta^{-13}C$  by a nonbonded interaction of the halogen atoms in the three-carbon fragment CF<sub>2</sub>CH<sub>2</sub>CHI, just as the shift of the CF<sub>2</sub>I signal downfield after substitution of the iodine atom by Alk should be not greater than 7 ppm. The observed change of ~40 ppm is apparently entirely associated with geminal nonbonded interactions of the iodine and fluorine atoms. The influence of the X substituents on the  $\delta$   $^{13}\text{C}$  of the fluoro-substituted carbon atoms in trans-fluoroolefins (Ia), (IIa), and (IIIa) (Table 3) is transmitted noticeably through four C-C bonds, which can be explained by participation of the double bond in the transmission of electronic effects. Thus, the signal of the first methylene carbon atom in the X substituent is at ~42 ppm for all adducts which do not have multiple bonds within two C-C bonds from the C atom, which is  $\sim 20$  ppm lower than the value calculated by the additive scheme [6, 7] without calculation of the influence on the  $\delta$  <sup>13</sup>C of nonbonded halogen interactions.

## EXPERIMENTAL

GLC analysis was carried out on a LKhM8-MD5 instrument with catharometer with temperature programming from 35 to 220°C ( $16^{\circ}C/min$ ). The following columns were used: 1) 1000 × 3 mm with 20% SKTFT-50 on N-AW chromaton (0.16-0.20 mm), 2) 1000 × 3 mm with 15% Carbowax 20 M on N-AW-HMDS chromaton (0.16-0.20 mm). There was good agreement in yields of the products obtained by distillation of the reaction mixture and those determined by GLC. <sup>13</sup>C NMR spectra were obtained for each substance (TMS as internal standard) on a Bruker WP-200-SY spectrometer (50, 31 MHz) using the Gmodecho technique (with proton decoupling and with inverted phase for signals of C atoms bound to an even or uneven number of protons).

All experiments on addition of (Ia-g) to 1-hexene and methyl acrylate were carried out in sealed glass ampuls (6  $cm^3$ ) with rotation stirring. In Tables 1 and 2 reaction conditions (reagent amounts, time, temperature), iodide conversions, and yields of adducts formed are shown. Characteristics of the adducts are shown in Table 4. <u>Reaction of F0<sub>2</sub>SOCF<sub>2</sub>CF<sub>2</sub>I (If) with Fe(CO)<sub>5</sub></u>. A mixture of 0.652 g (2 mmoles) of compound (If) and 0.392 g (2 mmoles) of Fe(CO)<sub>5</sub> was heated for 15 min at 140°C. There was obtained 0.5 g (89%) of IFeOSO<sub>2</sub>F as solid brown substance, infusible to 250°C and insoluble in organic solvents. Found: Fe 19,27; S 10.98; F 6.51%. FFeIO<sub>3</sub>S. Calculated: Fe 19.82; S 11.38; F 6.74%.

#### CONCLUSIONS

l. Fluoroaliphatic iodides containing electron-accepting substituents in the  $\alpha$ -position homolytically add to double bonds with cleavage of the C-I bond upon thermal, peroxide, or metallocomplex initiation.

2. Di-tert-butylperoxide and the  $Fe(CO)_5$ -DMF system initiate effectively addition of  $(CF_9)_2CFCF=CFCF_2I$ ,  $ICF_2CN$ ,  $ICF_2COOCH_3$ ,  $CF_3CF_2CF_2I$ ,  $CF_3(CF_2)_4CF_2I$ ,  $ICF_2CF_2OSO_2F$ , and  $(CF_3)_2-CFOCF_2CF_2I$  to 1-hexene.

3. Addition to methyl acrylate takes place only with the most reactive addends,  $(CF_3)_2CFCF=CFCF_2I$  and  $ICF_2CN$ .

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# POLAR CONTROL IN THE REMOTE OXIDATIVE FUNCTIONALIZATION

OF SULFONES

É. I. Troyanskii, M. I. Lazareva, D. V. Demchuk, and G. I. Nikishin UDC 542.943.7:547.279.53

By rearrangement with 1,5- and 1,6-migration of the hydrogen of oxygen- and nitrogencentered radicals and cation-radicals, generated by one-electron oxidation, we have developed a general method for the single-step remote oxidative functionalization of organic compounds at the unreactive  $\gamma$ - or  $\delta$ -carbon atoms [1]. Using this method in systems containing sodium peroxydisulfate, remote functionalization of carboxylic acids and their amides [2], ketones [3, 4], and various types of sulfonamides [1, 5, 6] has been achieved. The possibility of effecting remote functionalization in these reactions is governed by the presence of unpaired electrons in the groups C(0)0<sup>°</sup>, C(0)NH, C=0<sup>+</sup>, and SO<sub>2</sub>NR<sup>1</sup>.

We have now examined the oxidation of dialkyl sulfones in systems containing  $Na_2S_2O_8$ , with a view to the possible use of the sulfonyl group  $SO_2$  as an activator of remote functionalization. We have found that the dialkyl sulfones (I) on oxidation with an excess of  $Na_2S_2O_8$  [(I): $Na_2S_2O_8$  = 1:2-4] are selectively converted into the 3-oxosulfones (II). When the amount of oxidant is reduced, in addition to (II) the 3-hydroxysulfones (IIIa, c) are formed. The use of large amounts of  $Na_2S_2O_3$  also clearly results in side reactions involving more extensive oxidation, which are in part responsible for the low yield of (IIb) from

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