Reactions of Olefinic Double Bonds with Polyfluoroalkyl Radicals Generated Electrochemically

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Summary The addition of polyfluoroalkyl radicals, generated electrochemically, to olefinic double bonds, illustrates a new method of obtaining a number of novel polyfluoroalkyl derivatives.

SEVERAL methods are available[1] for the introduction of polyfluoroalkyl radicals into organic systems. In most cases, however, the counter radical, *e.g.* I from R_fI, is also introduced. We now report a new approach, for the introduction of polyfluoroalkyl radicals, involving electrochemistry of fluorinated acids.

The Kolbe electrolysis of fluorocarbon acids is known to yield the expected dimers,[2] and in the few reports available there has been little evidence for the side products often found in electrolysis of hydrocarbon acids, probably due to the difficulty of generating polyfluoroalkyl carbonium ions. Recently some reports of crossed Kolbe reactions between hydrocarbon and fluorocarbon acids have appeared but difficulties were encountered due to differing acidities of the reactants.[3]

The method used here is based on electrolysis of polyfluoroacids, in an acetonitrile–water system in the presence of unsaturated substrates. The general reaction is summarised in Equation (1). The amounts of each product obtained depend on the nature of the group X and the reaction conditions. Under the conditions we have used the dimer (V) usually predominates. The results obtained

$$R_f{\cdot}CO_2H + CH_2 = CHX \rightarrow \underset{(I)}{R_fCH_2CH_2X} + \underset{(II)}{R_fCH{=}CHX}$$

$$+ \underset{(III)}{R_fCH_2{\cdot}CH{=}CHY} + \underset{(IV)}{R_fCH_2CHXR_f}$$

$$+ \underset{(V)}{R_f{\cdot}CH_2CHXCHXCH_2R_f} \qquad (1)$$

$R_f = CF_3$; C_2F_5; C_3F_7; C_7F_{15} $X = CO_2Me$; alkyl; CN
$Y = X - CH_2$ when X = alkyl.

TABLE 1

Fluoroalkylation of olefins using CF_3COOH

	Product (X = alkyl) yield %				
Olefin	(I)	(II)	(III)	(IV)	(V)
$CH_2{=}CH(CH_2)_2CH_3$	13·2	4·4	2·2	—	39·6
$CH_2{=}CH(CH_2)_3CH_3$	12·5	7·5	7·5	trace	22·5
$CH_2{=}CH(CH_2)_4CH_3$	15	6	6	,,	26

$HC{\equiv}3(CH_2)_3CH_3$, $CF_3CH{=}CH(CH_2)_3CH_3$ and *cis*-$CF_3CH{=}C$-$CF_3(CH_2)_3CH_3$. 1:1 10% yield.

[a] Structures determined by i.r., ^1H and ^{19}F n.m.r., m.s. and elemental analysis.

with various acids and olefins and an acetylene are summarised in Tables (**1**) and (**2**).

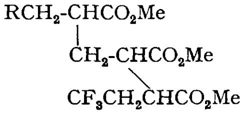
TABLE 2

Fluoroalkylation of olefin acids and nitriles

Olefin	Products	Yield % where R_f = CF_3	C_2F_5	n-C_3F_7	n-C_7F_{15}
$CH_2=CHCO_2Me$ ..	(I)	5	4·5	3	trace
	(II)		55		
	(IV)	5	15	14	trace
	(V)	50	35	36	34
	(VI)	10[c]			
$CH_2=CHCN$	(I)	5			
	(VI)	30		18	
$CH_2=CH-CH_2CO_2Me$	(I)	12			
	(II)[b]	5			
	(III)	5			
	(V)	25			

[a] Structure determined by i.r., ^1H and ^{19}F n.m.r., m.s. and elemental analysis.

[b] *Trans*-isomer.

[c]


Several points of interest are shown. Kolbe electrolysis of hydrocarbon acids (RCO_2H) in the presence of dienes, *e.g.* butadiene[4] and conjugated monoenes *e.g.* methyl acrylate[5] is known and gives reasonable yields of dimers, *e.g.* $(RCH_2CHCOOEt)_2$, but generally only low yields of hydrogen abstracted products RCH_2CH_2COOEt or olefins $RCH=CHCOOEt$ corresponding to our products (I—IV) are found. Addition to alkenes, *e.g.* $CH_2=CHC_4H_9$ gives only low yields of disubstituted products of the type $RCH_2CHRC_4H_9$.[6] In most of our reactions the total yields of adducts both to olefins and olefin acids are reasonable (37—60%). The reactions are clean and in most cases little polymerisation occurs. In reactions[1] of polyfluoroalkyl radicals reported previously, the telomeric products are of the type $R_fCH_2CHX{\cdot}CH_2CHXY$ (X = H, alkyl, CO_2Me, *etc.*; Y = H or I), *i.e.* products derived from the reaction of the first formed adduct $R_fCH_2CHX\cdot$ with more monomer, followed by abstraction of iodine from R_fI or by hydrogen abstraction, to give head to tail products. In our case, head to head dimers are obtained and a likely route is dimerisation of the first formed radicals, which are concentrated round the electrode and not uniformly distributed in the medium; (Equation (**2**)]. In one case

$$2R_fCH_2CHX\cdot \rightarrow R_fCH_2CHXCHX\,CH_2R_f \tag{2}$$

(CF_3COOH and $CH_2=CHCO_2Me$) a small quantity of a telomer (VI) was formed as well as the dimer. The dimer was the same as in other reactions, *i.e.* head to head, but the telomer resulted from head to tail addition.

The electrolysis was carried out in a divided cell, the olefinic substrate being placed in the anode compartment. The scale of the reactions was in the range 10—50 mmol olefin and 30—150 mmol acid in *ca.* 200 cm^3 acetonitrile water (8 : 1) containing *ca.* 5—15 mmol sodium hydroxide. A platinum sheet (2·5 cm^2) was used as anode, at a potential of >20·0 V and a current of *ca.* 1 A.

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[1] J. M. Tedder and J. C. Walton, *Progr. Reaction Kinetics*, 1967, **4**, 53; N. O. Brace, *J. Org. Chem.*, 1967, **32**, 430.

[2] A. I. Levin, O. N. Chechina, and S. V. Soholov, *Zhur. obshchei. Khim*, 1969, **39**, 413.

[3] R. N. Renaud and D. E. Sullivan, *Canad. J. Chem.*, 1973, **51**, 772.

[4] R. V. Lindsey and M. L. Peterson, *J. Amer. Chem. Soc.*, 1959, **81**, 2073.

[5] M. Chkir and D. Lelandais, *Chem. Comm.*, 1971, 1369.

[6] H. Schafer and R. Pistorius, *Angew. Chem. Internat. Edn.*, 1972, **11**(**9**), 841.