Preliminary Note

Direct hydroperfluoroalkylation of ethyl propiolate with perfluoroalkyl iodides and bromides by a Co/Zn bimetal redox system

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Abstract

The addition of perfluoroalkyl halides R_fX (**1**) (X = I, Br) to ethyl propiolate (**2**) has been performed smoothly with zinc powder and a catalytic amount of bromo(pyridine)cobaloxime(III) (**3**) in ethanol. The product (**4**) was a mixture of *Z*- and *E*-isomers, with the former predominating.

The introduction of per(poly)fluoroalkyl groups into organic molecules is of great use in industry as well as in the laboratory [1]. The perfluoroalkylation of alkynes has been extensively studied for this purpose during the past years [2]. The products thus formed still contain a double bond capable of further reaction [2a, 3]. Due mainly to the electron-deficiency of the perfluoroalkyl radical $R_f\cdot$, there are few reports about the perfluoroalkylation of electron-deficient carbon–carbon multiple bonds such as those in acrylates [4] and propiolates [2e].

In a previous paper [5] we described a bimetal redox system, *i.e.* **bromo(pyridine)cobaloxime(III) (3)**/zinc powder (see p. 114), which was able to promote the addition of perfluoroalkyl iodides to acrylates. Further studies on this redox couple show it could similarly initiate the direct hydroperfluoroalkylation of ethyl propiolate (**2**) with perfluoroalkyl halides R_fX (**1**) (X = I, Br). The results obtained are shown in Table 1.

$$\underset{(1)}{R_fX} + \underset{(2)}{CH{\equiv}CCO_2Et} \xrightarrow{\text{Cobaloxime(3)/Zn}} \underset{(4)}{R_fCH{=}CHCO_2Et}$$

(**1a**: $R_f = ClC_4F_8$, X = I; **1b**: $R_f = ClC_6F_{12}$, X = I; **1c**: $R_f = C_4F_9$, X = I; **1d**: $R_f = C_6F_{13}$, X = I; **1e**: $R_f = ClC_6F_{12}$, X = Br; **1f**: $R_f = C_6F_{13}$, X = Br; **1g**: $R_f = C_8F_{17}$, X = Br)

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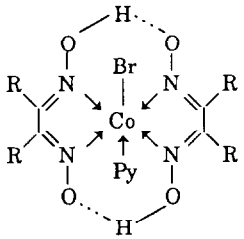

$C_{13}H_{19}BrCoN_5O_4$, when $R = CH_3$

TABLE 1

Hydroperfluoroalkylation of propiolate (2) with R_fX (1) initiated by the Co/Zn redox couple[a]

Entry	R_fX (1)	Temp. (°C)	Time (h)	Product (4)[b] (*E*:*Z*[c])	Yield[d] (%)
1	(**1a**)	25	8	$ClC_4F_8CH{=}CHCO_2Et$ (**4a**) (26:74)	85.2
2	(**1b**)	25	5	$ClC_6F_{12}CH{=}CHCO_2Et$ (**4b**) (13:87)	81.8
3	(**1c**)	20	7	$C_4F_9CH{=}CHCO_2Et$ (**4c**) (9:91)	73
4	(**1d**)	25	5	$C_6F_{13}CH{=}CHCO_2Et$ (**4d**) (14:86)	82.5
5	(**1e**)	25	8	$ClC_6F_{12}CH{=}CHCO_2Et$ (**4b**) (25:75)	71
6	(**1f**)	30	7	$C_6F_{13}CH{=}CHCO_2Et$ (**4d**) (30:70)	76
7	(**1g**)	30	10	$C_8F_{17}CH{=}CHCO_2Et$ (**4e**) (28:72)	65

[a]Molar ratio of (**1**):(**2**):Zn:(**3**) = 3:1:4.5:0.02 (when X = I) or 1:1:1.5:0.02 (when X = Br).
[b]The structure of (**4**) was characterized by MS, IR, ^1H NMR, ^{19}F NMR and microanalyses.
[c]Estimated by GLC.
[d]Isolated yield based on (**2**).

As shown in Table 1, the reaction was performed at ambient temperature and usually completed within a few hours. Excess reactants (**1**) were necessary for the complete conversion of (**2**) in the case of iodides [(**1a**)–(**1d**)], as a considerable amount of (**1**) was converted to R_fH. The adduct (**4**) thus formed was a hydroperfluoroalkylation product of (**2**) such compounds being previously obtained by the Pd-catalyzed perfluoroalkylation and carbo-carbonylation reactions [6]. It consisted of a mixture of *Z*- and *E*-isomers, with the former predominant.

In the absence of (**3**), no hydroperfluoroalkylation adduct (**4**) could be isolated in parallel experiments.

Experimental

General procedure

A suspension of Zn powder and cobaloxime (**3**) in EtOH [*ca.* 3 ml mm^{-1}(**1**)] was stirred under N_2 for more than 0.5 h. When the reaction mixture turned green, (**2**) and (**1**) were added dropwise over 0.5 h. The slurry so formed was stirred for several hours (see Table 1). After that the mixture was poured onto ice/water and filtered. The filtrate was extracted with ether. Usual workup gave the corresponding product (**4**).

Analyses

(**4a**): Calcd. for $C_9H_7ClF_8O_2$: C, 32.31; H, 2.11; F, 45.42%. Found: C, 31.53; H, 1.97; F, 47.53%. IR: 1740(CO_2Et), 1660(CH=CH)cm^{-1}. ^1H NMR(neat): δ(ppm) 5.54–7.44(m, 2H), 4.29(q, 2H, J=7.4 Hz), 1.32(t, 3H, J=7.4 Hz). ^{19}F NMR(neat): δ(ppm) −7.7(s, 2F), 34.2–41.5(m, 2F), 44.1(s, 2F), 47.3(s, 2F). MS: 335(M+1), 307, 289(M−OEt).

(**4b**): Calcd. for $C_{11}H_7ClF_{12}O_2$: C, 30.40; H, 1.62; F, 52.46%. Found: C, 30.20; H, 1.59; F, 51.98%. IR: 1740(CO_2Et), 1660(CH=CH)cm^{-1}. ^1H NMR(CCl_4): δ(ppm)5.40–7.44(m, 2H), 4.25(q, 2H, J=6.5 Hz), 1.30(t, 3H, J=6.5 Hz). ^{19}F NMR(CCl_4): δ(ppm) −9.5(s, 2F), 32.9–40.7(m, 2F), 43.6(s, 2F), 44.7(s, 4F), 46.3(s, 2F). MS: 435(M+1), 407, 389(M−OEt).

(**4c**): Calcd. for $C_9H_7F_9O_2$: C, 33.98; H, 2.22; F, 53.74%. Found: C, 34.09; H, 2.37; F, 54.15%. IR: 1740(CO_2Et), 1660(CH=CH)cm^{-1}. ^1H NMR(neat): δ(ppm) 5.35–7.30(m, 2H), 4.24(q, 2H, J=6.5 Hz), 1.28(t, 3H, J=6.5 Hz). ^{19}F NMR(neat): δ(ppm) 6.2(s, 3F), 34.9–44.0(m, 2F), 49.0(s, 2F), 50.7(s, 2F). MS: 319(M+1), 291, 273(M−OEt).

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