

Preliminary Note

Addition of 1,2-dihaloperfluoroalkanes to alkenes initiated by dichlorobis(π -cyclopentadienyl)titanium and iron

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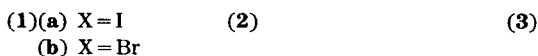
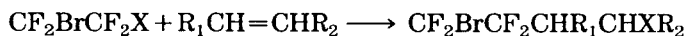
(Received July 2, 1991; accepted August 12, 1991)

Abstract

Addition of 1,2-dihaloperfluoroalkanes to various alkenes promoted by catalytic amounts of dichlorobis(π -cyclopentadienyl)titanium(IV) Cp_2TiCl_2 and iron powder gives 1:1 adducts in excellent yields. The reaction is performed in protic solvent (EtOH) without dehalogenation. A radical chain mechanism initiated by chlorobis(π -cyclopentadienyl)-titanium(III) $\text{Cp}_2\text{Ti(III)Cl}$ is proposed.

Recent exploration of radicals generated by the reaction of $\text{Cp}_2\text{Ti(III)Cl}$ with epoxides has proved promising [1]. Kitazume and Ishikawa studied the ultra-sound promoted perfluoroalkylation of enamines in the presence of zinc powder and a catalytic amount of Cp_2TiCl_2 , assuming $\text{Cp}_2\text{Ti(II)}$ to be the actual catalyst [2]. However, zinc is unsuitable for 1,2-dihaloperfluoroalkanes (1) because dehalogenation occurs prior to polyfluoroalkylation. Fuchikami and Ojima used air- and moisture-sensitive transition metal carbonyls to initiate the polyfluoroalkylation of alkenes [3]. We now report that iron can reduce Cp_2TiCl_2 to the greenish $\text{Cp}_2\text{Ti(III)Cl}$ and that such a new redox couple is capable of mediating the polyfluoroalkylation of alkenes (2) with (1).

In the presence of 30 mol% iron powder and 2 mol% Cp_2TiCl_2 , (1) and (2) reacted in EtOH under nitrogen. Usual workup gave adducts (3) in excellent yields. Representative results are shown in Table 1.

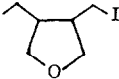
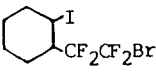
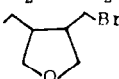
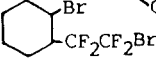


In the present system, neither the dehalogenation nor the hydrodehalogenation product ($\text{CF}_2=\text{CF}_2$ nor $\text{CF}_2\text{BrCF}_2\text{H}$, respectively) was detected

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TABLE 1

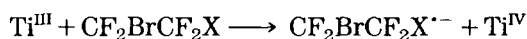
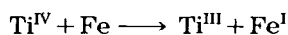
Addition of (1) to alkenes (2) initiated by Cp_2TiCl_2 and Fe^a

Run No.	(1)	Alkene (2)	Temp. (°C)	Time (h)	Adduct (3)	Yield ^b (%)
1	(1a)	1-octene	55	10	$\text{CF}_2\text{BrCF}_2\text{CH}_2\text{CHIC}_6\text{H}_{13}$	96
2		1-octene	55	15	$\text{CF}_2\text{BrCF}_2\text{CH}_2\text{CHIC}_6\text{H}_{13}$	91 ^c
3		allyl alcohol	65	13	$\text{CF}_2\text{BrCF}_2\text{CH}_2\text{CHICH}_2\text{OH}$	96
4		diallyl ether	55	7	CF_2BrCF_2 	94
5		cyclohexene	65	24		92
6	(1b)	1-octene	55	15	$\text{CF}_2\text{BrCF}_2\text{CH}_2\text{CHBrC}_6\text{H}_{13}$	95
7		1-octene	55	24	$\text{CF}_2\text{BrCF}_2\text{CH}_2\text{CHBrC}_6\text{H}_{13}$	0 ^c
8		1-hexene	60	15	$\text{CF}_2\text{BrCF}_2\text{CH}_2\text{CHBrC}_4\text{H}_9$	93
9		1,5-hexadiene	60	26	$\text{CF}_2\text{BrCF}_2\text{CH}_2\text{CHBrC}_2\text{H}_4\text{CH}=\text{CH}_2$	78
10		diallyl ether	60	8	CF_2BrCF_2 	95
11		cyclohexene	70	36		92

^aMolar ratio: (1):(2):Fe:Cp₂TiCl₂ = 1:1:0.3:0.02.^bIsolated yield based on (1). Satisfactory analytical and spectral data were obtained for all adducts.^cAbsence of Cp₂TiCl₂.

even in a protic solvent (EtOH). It was not necessary to use excess (1) for obtaining 1:1 adducts, the adducts (3) (still containing a reactive center —CF₂Br) once formed being stable enough to further reaction. Exclusively high regioselectivity was observed in the reaction of (1a) with (2). Cyclic tetrahydrofuran derivatives were formed with diallyl ether as the substrate (runs 4 and 10).

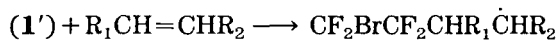
Iron alone was similarly capable of initiating the addition of (1a) to (2) (run 2), but Cp₂TiCl₂ was indispensable in the case of (1b) (run 7). Cp₂TiCl₂ itself could not initiate the reaction, but we have found that low-valent titanium, *i.e.* TiCl₃, can initiate a similar reaction [4]. The above addition was assumed to proceed through a radical chain mechanism (Scheme 1). In the case of (1a), a simple SET process may also explain the formation of the 2-bromotetrafluoroethyl radical (1') [5] as shown in Scheme 2. Further study on this system is in progress.



(1)

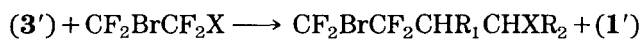


(1')



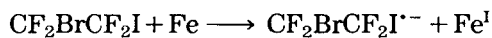
(2)

(3')



(3)

Scheme 1.



(1a)



(1')

Scheme 2.

References

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- 4 C.-M. Hu and Y.-L. Qiu, unpublished results.
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