

Addition of tetrachloromethane to trifluoroethene catalyzed by copper complexes

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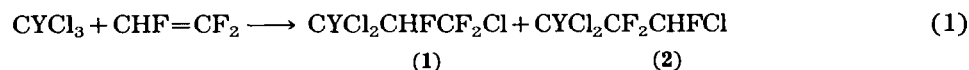
Abstract

The addition of tetrachloromethane to trifluoroethene catalyzed by copper complexes gives 1:1 adducts in up to 97% yield under mild reaction conditions. The catalytic activity and the regioselectivity of copper, ruthenium and palladium complexes and dibenzoyl peroxide have been compared. Differences in regioselectivity indicate that the copper-coordinated trichloromethyl radical is involved in copper-assisted addition reactions, whilst free-radical species in an uncomplexed form play a role in other cases.

Introduction

During the last 40 years attention has been paid to radical additions of polyhalogenated compounds including CCl_4 [1-7], CHCl_3 [3], CCl_3COOEt [5], CCl_3Br [7-9], CF_2ClCFCl and $\text{CF}_2\text{BrCFClBr}$ [10] to fluorosubstituted olefins, giving 1:1 adducts of synthetic interest. These radical additions were initiated by organic peroxides or catalyzed by CuCl [5, 6], FeCl_3 [4] and $\text{Fe}(\text{CO})_5$ [1]. To date, trifluoroethene has been little studied in addition reactions for synthetic purposes. Only three examples of the additions of CF_2ClCFCl , $\text{CF}_2\text{BrCFClBr}$ [10] and CF_2Br_2 [11] to trifluoroethene have been reported. The free-radical addition of CCl_3Br [12] initiated by UV radiation has also been reported, but the reaction conditions have not been presented in detail. Moreover, trifluoroethene is widely used in kinetic and regioselectivity studies of the addition reactions of halogenated alkyl radicals [13]. The results obtained from the kinetic studies demonstrate the very low reactivity of trifluoroethene in radical additions in comparison with other fluoroethenes.

Generally, the addition of polyhalogenated compounds to trifluoroethene leads to the formation of two regioisomers **1** and **2** [12, 13] [eqn. (1)] depending on differences in steric hindrance at CHF (A position) and CF_2 (B position) in trifluoroethene.



However, in the addition of CF_2ClCFCl , $\text{CF}_2\text{BrCFClBr}$ [10] and CF_2Br_2 [11], the formation of only one regioisomer has been reported. This was later explained by the inadequate analytical methods used [13].

The copper amine complexes $\text{Cu(L)}_n\text{Cl}$ ($\text{L} = \text{amine}$, $n = 1-2$) are known to be efficient catalysts for the additions of polyhalogenated compounds (CCl_4 ; CHCl_3 , etc.) [14, 15] to olefins. The aim of the present study was to examine further their catalytic activity and regioselectivity. The addition of tetrachloromethane to trifluoroethene, giving a 1:1 adduct as a mixture of two regioisomers, has been studied as the model reaction. The catalytic efficiencies of palladium [16, 17] and ruthenium [18, 19] complexes, also known as catalysts for the addition of tetrachloromethane to alkenes, and of dibenzoyl peroxide, an initiator of free-radical addition, have been examined as well.

Experimental

GC analysis was performed on HP-5890A with an HP Ultra-1 capillary column. Mass spectra were measured on Shimadzu QP-100 and VG Analytical mass spectrometers. Product yields were calculated from GC data using an internal standard (n-octane).

Materials

Tetrachloromethane (Lachema, Brno), n-butylamine, 2-methylpropylamine, n-propylamine, benzylamine (Fluka, Buchs) were distilled prior to use. 1-Bromo-2-chloro-1,2,2-trifluoro-ethane was kindly provided by Léciva-Dolní Měcholupy. Anhydrous 1,10-phenanthroline was obtained by heating phenanthroline monohydrate *in vacuo* at 100 °C for 8 h. The other chemicals were used as obtained.

Preparation of trifluoroethene

A 1 l three-necked flat bottom flask equipped with magnetic stirrer bar, dropping funnel and reflux condenser connected through a gas outlet with a dry ice condenser was charged with 400 ml of 2-propanol and Zn dust (130.7 g, 2 mol) activated by 1 ml of glacial acetic acid. The vigorously stirred mixture was refluxed, and $\text{CF}_2\text{BrCHFCl}$ (394.8 g, 2 mol) was added dropwise slowly, to avoid the vigorous formation of trifluoroethene. The trifluoroethene formed was condensed in the dry ice condenser and stored in a 0.5 l steel cylinder.

Addition reaction catalyzed by CuCl-amine complexes

Trifluoroethene (2.05 g, 0.025 mol) was condensed into a 60 ml glass ampoule equipped with a septum and a magnetic stirrer and then tetrachloromethane (50 ml), n-octane (0.0114 g, 0.0001 mol) as the internal standard and finally CuCl (0.1237 g, 0.00125 mol) were added. The ampoule was heated to 80 °C and a portion of amine (0.00250 mol) was injected through the septum. During the next 8 h another portion of amine (0.021 mol) was continuously added to the reaction mixture. After this time the

reaction mixture was washed with 50 ml of 10% aqueous HCl and the organic layer separated, dried with anhydrous CaCl_2 and subjected to GC and MS analysis. The yields and ratio of regioisomers are presented in Table 1.

$\text{CCl}_3\text{CFHCF}_2\text{Cl}$ (**3**). MS *m/e* (rel. int.): $\text{C}_2\text{HCl}_3\text{F}_3$ 199(4.9); CCl_3 117(73.4); $\text{C}_2\text{HCl}_2\text{F}$ 114(20.7); CF_2Cl 85(100); CCl_2 82(11.1); CF 31(21.5).

$\text{CCl}_3\text{CF}_2\text{CHFCl}$ (**4**). MS *m/e* (rel. int.): $\text{C}_2\text{HCl}_3\text{F}_3$ 199(42.5); $\text{C}_2\text{Cl}_2\text{F}_2$ 132(12.1); CCl_3 117(100); CCl_2 82(12.1); CHFCl 67(73.8); CFH 32(13.6); CF 31(23.5).

Addition reaction catalyzed by CuCl–phenanthroline complexes

Trifluoroethene (2.05 g, 0.025 mol) was condensed into a 60 ml glass ampoule equipped with a septum and a magnetic stirrer and then tetrachloromethane (50 ml), n-octane (0.0114 g, 0.0001 mol) as the internal standard and finally CuCl (0.1237 g, 0.00125 mol) were added. The ampoule was heated to 80 °C and phenanthroline or phenanthroline monohydrate (0.00250 mol) dissolved in 5 ml of tetrachloromethane was injected through the septum. After 8 h the reaction mixture was washed with 50 ml of 10% aqueous HCl and the organic layer separated, dried with anhydrous CaCl_2 and subjected to GC and MS analysis. No reaction products were found in the reaction mixture.

Addition reaction initiated by dibenzoyl peroxide

Trifluoroethene (2.05 g, 0.025 mol) was condensed into a 60 ml glass ampoule equipped with a septum and a magnetic stirrer, and then tetrachloromethane (50 ml), n-octane (0.0114 g, 0.0001 mol) as the internal standard and finally dibenzoyl peroxide (0.303 g, 0.00125 mol) were added. The ampoule was heated to 80 °C for 8 h. The reaction mixture was then subjected to GC and MS analysis. The yield of regioisomers **3** and **4** was 14.4%.

$\text{CCl}_3(\text{CFHCF}_2)_2\text{Cl}$ (**5**). MS *m/e* (rel. int.): $\text{C}_5\text{H}_2\text{F}_6\text{Cl}_3$ 281(80); $\text{C}_5\text{HF}_6\text{Cl}_2$ 245(18); $\text{C}_4\text{H}_2\text{F}_6\text{Cl}$ 199(34); $\text{C}_3\text{HF}_5\text{Cl}$ 167(19); CCl_3 117(100); CF_2Cl 85(58).

$\text{CCl}_3(\text{CFHCF}_2)_3\text{Cl}$ (**6**). MS *m/e* (rel. int.): $\text{C}_7\text{H}_3\text{F}_9\text{Cl}_3$ 363(42); $\text{C}_5\text{H}_2\text{F}_8\text{Cl}_2$ 249(38); $\text{C}_3\text{HF}_5\text{Cl}$ 167(23); CCl_3 117(100); CF_2Cl 85(82).

CCl_3CCl_3 (**7**). MS *m/e* (rel. int.): C_2Cl_5 199(50); C_2Cl_4 164(23); C_2Cl_3 129(15); CCl_3 117(100); C_2Cl_2 94(28); CCl_2 82 19(19).

Addition reaction catalyzed by $\text{RuCl}_2(\text{PPh}_3)_3$

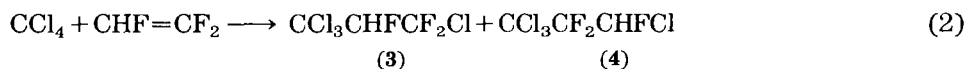
Trifluoroethene (2.05 g, 0.025 mol) was condensed into a 60 ml glass ampoule equipped with a septum and a magnetic stirrer, and then tetrachloromethane (50 ml), n-octane (0.0114 g, 0.0001 mol) as the internal standard and finally $\text{RuCl}_2(\text{PPh}_3)_3$ (0.2397 g, 0.00025 mol) were added. The ampoule was heated to 80 °C for 8 h. The reaction mixture was then filtered through a small amount of silica gel to remove the catalyst and subjected to GC and MS analysis. No reaction products were found in the reaction mixture.

Addition reaction catalyzed by Pd(OAc)₂

Trifluoroethene (2.05 g, 0.025 mol) was condensed into a 60 ml glass ampoule equipped with a septum and a magnetic stirrer, and then tetrachloromethane (50 ml), n-octane (0.0114 g, 0.0001 mol) as the internal standard and finally Pd(OAc)₂ (0.0561 g, 0.00025 mol), PPh₃ (0.131 g, 0.0005 mol) and K₂CO₃ (0.0691 g, 0.0005 mol) were added. The ampoule was heated to 80 °C for 8 h. The reaction mixture was then filtered through a small amount of silica gel to remove the catalyst and subjected to GC and MS analysis. The yield of regioisomers **3** and **4** was 2.7%.

Results and discussion

In general, the addition of tetrachloromethane to trifluoroethene results in all cases in the formation of two regioisomers **3** and **4** (eqn. (2)) as expected. The regioisomer **3** prevails due to a preferential attack on the less sterically hindered position A (CHF). The results are presented in Table 1.



Addition reaction catalyzed by copper complexes

Copper complexes with amines as ligands exhibited much higher catalytic activity than the other catalysts used (Table 1). The best results were obtained with 2-methylpropylamine (97.0%), n-butylamine (86.4%) and propylamine (69.9%) as the ligands. It is worth mentioning that the 1:1 adducts **3** and **4** are the only products of the addition reaction. Telomers were not formed when copper amine complexes were used as the catalysts.

The CuCl–phenanthroline complex which is known to catalyze efficiently the addition of chloroform to styrene [14] was inactive in this case.

TABLE 1

Yield of 1:1 adducts and ratio of regioisomers **3** and **4** in addition of tetrachloromethane to trifluoroethene

Catalyst	Ratio 3 : 4	Yield (%)
Cu(L) _n Cl, L = amine		
propylamine	2.19	69.9
n-butylamine	2.48	86.4
2-methylpropylamine	2.39	97.0
benzylamine	2.48	23.5
1,10-phenanthroline·H ₂ O	–	0.0
1,10-phenanthroline	–	0.0
Pd(OAc) ₂ + 2PPh ₃ + 2K ₂ CO ₃	4.92	2.7
RuCl ₂ (PPh ₃) ₃	–	0.0
Bz ₂ O ₂	4.67	14.4

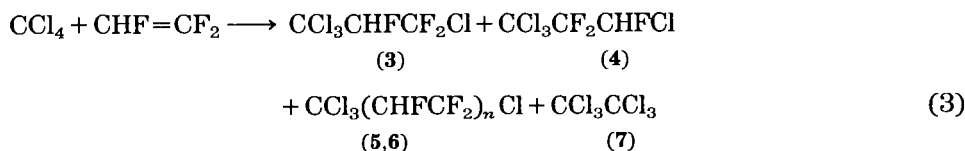
The most interesting results concern the different 3:4 ratios in the copper-catalyzed addition reactions relative to those with dibenzoyl peroxide or the Pd catalyst, respectively. These preliminary results indicate the possibility of a catalyst effect on the regioselectivity of the addition reaction. This can be explained by the coordination of trifluoroethene and the trichloromethyl radical by the copper catalyst. Whilst under free-radical conditions (dibenzoyl peroxide) the possibilities for a variation in the regioselectivity are rather limited (*e.g.* solvent effect), it seems that in true catalytic addition reactions the metal-radical interaction may play an important role. A study of this subject, including ligand effects, is in progress.

Addition reaction catalyzed by ruthenium and palladium complexes

Complexes of palladium [Pd(OAc)₂ + 2PPh₃ + 2K₂CO₃] [16, 17] and ruthenium [RuCl₂(PPh₃)₃] [18, 19] are known to be excellent catalysts for the addition of tetrachloromethane to alkenes. However, in our case they were found to be inactive; RuCl₂(PPh₃)₃ was completely inactive and the system Pd(OAc)₂ + 2PPh₃ + 2K₂CO₃ exhibited only a slight catalytic effect, affording a 1:1 adduct in only 2.7% yield. Similar behaviour for Ru and Pd catalysts was observed in the addition of tetrachloromethane to chlorotrifluoroethene [20]. These results indicate that palladium and ruthenium compounds are not general catalysts for the addition of polyhalogenated compounds to olefins.

Addition reaction initiated by dibenzoyl peroxide

It is known that peroxide-induced additions proceed through a free-radical chain mechanism and that the formation of 1:1 adducts is always accompanied by the formation of telomers [21–23]. The addition initiated by dibenzoyl peroxide has therefore been performed for the purpose of comparison with the results obtained in the metal-catalyzed additions. The total yield of 1:1 adducts **3** and **4** was rather low (14.4%) because of side reactions. Telomers **5** and **6** (*n* = 2, 3) and hexachloroethane **7**, which is formed by dimerization of the trichloromethyl radical, were also found in the reaction mixture [eqn. (3)]. GC analysis of the reaction mixture showed that other compounds are present too, but an attempt to determine their structure failed.



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