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Studies on the preparation of 2-(trifluoromethyl)acrylic acid and its esters from 3,3,3-trifluoropropene via hydrocarbonylation reactions

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Abstract

The synthesis of methyl α-(trifluoromethyl)acrylate (MTFMA) has been carried out in three steps starting from commercially available 3,3,3,-trifluoropropene; this route involving the cobalt-catalyzed carbonylation of 2-bromo-3,3,3-trifluoropropene (2-Br-TFP) under very mild reaction conditions, gave only about 30% yield of the desired methyl ester. 2-(Trifluoromethyl)propanal, available in 90% yield by rhodium catalyzed hydroformylation of 3,3,3-trifluoropropene, proved to be an interesting starting product for the preparation of MTFMA: while the synthetic route involving the α-halogenation of 2-(trifluoromethyl)propanoic acid (TFMPA) failed to give any results, the reaction scheme based on the α-selenenylation of the above aldehyde followed by H_2O_2-oxidation afforded 68% yield of 2-(trifluoromethyl)acrylic acid (TFMAA). © 1997 Elsevier Science S.A.

Keywords: Fluorinated methacrylates; Catalytic hydrocarbonylation; Fluorinated monomers

1. Introduction

Polymers of fluorinated monomers, including polyacrylates, have rapidly found an increasing use in the areas of high performance coating and protective materials for various types of surfaces [1–3].

Consistent with our general interest in the preparation of new polymeric materials endowed with outstanding outdoor stability and suitable technological properties to be employed for building materials and conservation of monumental and historic structures [4–6], we have a project to develop a new and efficient method for the preparation of 2-(trifluoromethyl)acrylic acid (TFMAA) and its esters, valuable starting compounds for homo- and co-polymers having a definite fluorine content and distribution.

Various preparative routes to TFMAA and its derivatives are described in the literature [7–10]. The first of them is based on the conversion of 1,1,1-trifluoroacetone into 2-trifluoromethylacrylonitrile via thermal dehydration of the corresponding cyanohydrin followed by hydrolysis of the unsaturated nitrile to TFMAA: the overall yield did not exceed 40% [7].

Other methods utilize 2-bromo-3,3,3-trifluoro-1-propene (2-Br-TFP) as a starting material, readily accessible by bromine addition to commercially available 3,3,3-trifluoropropene (TFP) followed by controlled dehydrobromination in the presence of alcoholic potassium hydroxide [8]. Low temperature lithiation of 2-Br-TFP and successive reaction with CO_2 of the intermediate lithium derivative affords TFMAA in about 56% yield [9].

A more efficient method consists in the one-step hydrocarboxylation of 2-Br-TFP carried out at 40 atm carbon monoxide and 80 °C in the presence of $PdCl_2(PPh_3)_2$ as catalyst, triethylamine and water: the yield of TFMAA reaches about 70% [10].

In a previous paper [3] we reported some attempts to optimize this catalytic process with the aim obtaining directly esters from TFMAA. These represent the most convenient and reactive monomers for polymethylacrylates and are not easily accessible from the free acid through classical esterification methods: unfortunately, we were not able to carry out this reaction with satisfactory chemoselectivity. TFMAA is a commercially available compound: it is, however, only available in limited quantities and at very high price.

Herein, we report the preparation of TFMAA methyl ester starting from TFP and using two different strategies: (i) through the carbomethoxylation of 2-Br-TFP under very mild reaction conditions catalyzed by cobalt carbonyl complexes; (ii) by rhodium catalyzed hydroformylation of TFP to 2-

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methyl-3,3,3-trifluoropropanal followed by conversion of this aldehyde to the desired TFMAA ester.

2. Experimental

2.1. Materials

3,3,3-Trifluoropropene was purchased from Fluorochem Limited. 2-Bromo-3,3,3-trifluoropropene was prepared by 3,3,3-trifluoropropene bromination followed by dehydrobromination with KOH in ethanol [8]. Diphenyl diselenide was used as received from Fluka Chemie AG. 4-(Phenylseleno)morpholine was prepared by bromination of diphenyl diselenide and successive addition of morpholine [11]. $NaClO_2$ and H_2O_2 35% were Aldrich reagents. The catalytic precursors $Co_2(CO)_8$ [12] and $HRh(CO)(PPh_3)_3$ [13] were prepared following well-known procedures.

2.2. Carbonylation of 2-bromopropene and 2-Br-TFP [14]

In a flask equipped with magnetic stirrer, thermometer, dropping funnel and a condenser maintained at −25 °C and connected to a carbon monoxide burette were placed 15 ml of methanol, 1.85 g (25 mmol) of $Ca(OH)_2$ and 0.208 g (0.5 mmol) of $Co_2(CO)_8$ under a CO atmosphere. To this solution, kept at 25 °C, 1.2 g (10 mmol) of 2-bromopropene were added and then a solution of 3.15 g (25 mmol) of dimethyl sulfate in 15 ml of methanol was very slowly added (10 h) to the reaction mixture. Stirring was continued at 25 °C until CO absorption ceased. The conversion of 2-bromopropene, determined by GC analysis, was 63% (run 4 of Table 1) and the reaction products, methyl acrylate, dimethyl succinate and methyl acetate, were identified by comparing their GC–MS spectra with those of authentic samples.

When 2-Br-TFP was employed as the substrate, under the above reaction conditions, the total yield of the esters was 31%. GC–MS and ^1H NMR spectra of methyl-2-(trifluoromethyl)acrylate (MTFMA) and dimethyl 2-(trifluoromethyl)succinate were in agreement with those reported in literature [3].

2.3. Hydroformylation of 3,3,3-trifluoropropene [15]

A 150 ml stainless steel autoclave was charged with 91.8 mg (0.01 mmol) of $HRh(CO)(PPh_3)_3$, 20 ml of toluene, 12.6 g (130.7 mmol) of 3,3,3-trifluoropropene and then with hydrogen and carbon monoxide (1:1) up to 100 atm. The vessel was magnetically stirred and heated at 80 °C for 15 h. GC analysis of the reaction crude showed the formation of 2-(trifluoromethyl)propanal (95%) and 3-(trifluoromethyl)propanal (5%) in 90% yield. The reaction mixture was distilled under nitrogen atmosphere to give 13.2 g of 2-(trifluoromethyl)propanal (bp 60 °C). This aldehyde must be used immediately after its purification to avoid its rapid con-

Table 1
Carbomethoxylation of 2-Br-propene and 2-Br-(3,3,3-trifluoro)propene catalyzed by $Co_2(CO)_8$ in the presence of different bases and promoters

Entry	Substrate	Base	Promoter	Conv.(%)	A yield(%)	B yield(%)
1	CH_2=CBr–CH_3	$Ca(OH)_2$	$(CH_3O)_2SO_2$	27	100	0
2	CH_2=CBr–CH_3	$Ca(OH)_2$	$(CH_3O)_2SO_2$	30 [a]	87	13
3	CH_2=CBr–CH_3	$Ca(OH)_2$	$(CH_3O)_2SO_2$	24 [b]	80	20
4	CH_2=CBr–CH_3	$Ca(OH)_2$	$(CH_3O)_2SO_2$	63 [c]	97	3
5	CH_2=CBr–CH_3	K_2CO_3	$(CH_3O)_2SO_2$	16	100	0
6	CH_2=CBr–CH_3	CH_3ONa	$(CH_3O)_2SO_2$	0 [d]	–	–
7	CH_2=CBr–CH_3	$Ca(OH)_2$	Cyanuric chloride	0	–	–
8	CH_2=CBr–CH_3	$Ca(OH)_2$	Cyanuric chloride	0 [a]	–	–
9	CH_2=CBr–CH_3	$Ca(OH)_2$	$BrCH_2COOC_2H_5$	15 [e]	67	33
10	CH_2=CBr–CH_3	$Ca(OH)_2$	$BrCH_2COOC_2H_5$	11 [f]	55	45
11	CH_2=CBr–CH_3	$Ca(OH)_2$	$ClCH_2CN$	0 [d]	–	–
12	CH_2=CBr–CH_3	$Ca(OH)_2$	$BrCH_2CHF_2$	7 [c]	99	1
13	CH_2=CBr–CH_3	$Ca(OH)_2$	$(C_6H_5)_3CCl$	9 [c]	47	53
14	CH_2=CBr–CF_3	$Ca(OH)_2$	$(CH_3O)_2SO_2$	31 [c]	99	1

A = R–C(COOCH$_3$)–CH$_2$ B = R–CH(H$_3$COOC)–CH$_2$–COOCH$_3$ R = –CH_3 or –CF_3

Substrate = 10 mmol; $Co_2(CO)_8$ = 0.5 mmol; base = 25 mmol; promoter = 25 mmol; P = 1 atm; temperature = 25 °C; methanol = 15 ml.
[a] Temperature = 40 °C (some decomposition of cobalt catalyst is observed by formation of inorganic cobalt salts).
[b] Reaction carried out bubbling CO into the solution.
[c] The promoter was diluted in 20 ml of methanol and added over about 10 h.
[d] Extensive formation of inorganic cobalt salts was observed.
[e] 97% $BrCH_2COOCH_3$ was formed by transesterification with the promoter.
[f] Ethanol was used as the solvent.

version to its dimeric condensation product even at low temperature.

2.4. 2-(Trifluoromethyl)propanoic acid (TFMPA)

The reaction was carried out following an experimental procedure described by Dalcanale and Montanari [16].

To a solution of 15 g (119 mmol) of 2-(trifluoromethyl) propanal in 140 ml of acetonitrile and 3.8 g of NaH_2PO_4 in 56 ml H_2O and 14 ml (146 mmol) of 35% H_2O_2 was added a solution of 18 g (158 mmol) of $NaClO_2$ in 158 ml H_2O keeping the temperature at 10 °C by water cooling. During the reaction (about 2 h) oxygen is evolved and monitored with a bubbler connected to the apparatus. At the end of the reaction 1.43 g of Na_2SO_3 were added to destroy the unreacted HOCl and H_2O_2. The reaction mixture was then acidified with 10% aqueous HCl, extracted with diethyl ether and dried over Na_2SO_4. After distillation the pure acid TFMPA was obtained (bp 85 °C/10 mmHg) with 80% yield.

IR (KBr pellet): ν (cm^{-1}) 3500–3000 (OH), 1728 (C=O), 1468 (CH_3), 1250–1100 (CF_3). ^1H NMR ($CDCl_3$) δ (ppm): 9.6 (1H, –COO*H*), 3.3 (m, 1H, CF_3–C*H*–CH_3), 1.5 (d, 3H, –CH–C*H*$_3$). MS *m/e*: 142 (M^+); 125 ($M^+ - OH$); 122 ($M^+ - HF$); 77 (122 − COOH); 97 ($M^+ - COOH$); ($M^+ - CF_3$); 69 (CF_3); 45 (COOH).

2.5. 2-(Trifluoromethyl)acrylic acid (TFMAA) from 2-(trifluoromethyl)propanal

The product was prepared following a procedure described by Outurquin and Paulmier [17]

A solution of 0.8 g (5 mmol) of Br_2 in CH_2Cl_2 is slowly added to a stirred solution of 1.56 g (5 mmol) of diphenyl diselenide in 30 ml of CH_2Cl_2 at room temperature. When 1.90 g (20 mmol) of morpholine are added dropwise, the brown solution becomes pale yellow. To this solution are added dropwise, at 20 °C, 0.94 g (8.5 mmol) of the distilled 2-(trifluoromethyl) propanal and the reaction mixture stirred for 15 h. After this time 50 ml of HCl 1 N are added and the organic phase separated, washed with 40 ml H_2O and then 30% H_2O_2 solution in 20 ml THF at − 10 °C added dropwise. The mixture is stirred for 2 h at 0 °C and 10 h at room temperature; then 50 ml of H_2O are added and the organic phase is separated, washed with brine (2 × 20 ml) and dried with molecular sieves. The reaction mixture is distilled under vacuum to give 0.81 g (5.8 mmol) of TFMAA (bp 86 °C/35 mmHg) in 68% yield.

2.6. Methyl α-(trifluoromethyl)acrylate (MTFMA)

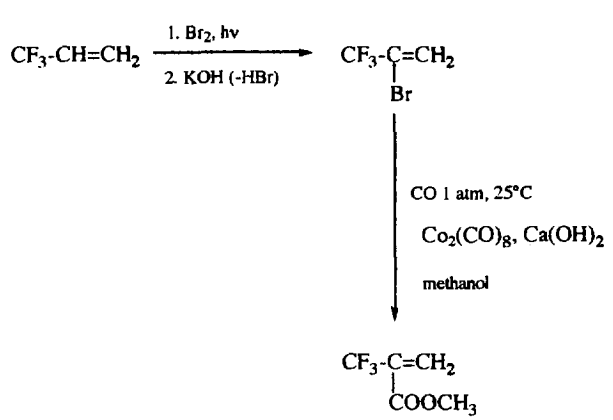
The reaction was performed following a procedure reported for analogous products [18].

A solution of 10 g (61.4 mmol) of TFMAA in 100 ml dry acetone, 12.6 (79.6 mmol) of dimethyl sulfate and 11 g of (79.6 mmol) K_2CO_3 previously dried and carefully triturated, is heated under reflux for 5 h. The solution is then decanted and the solid product washed with acetone: distillation from the acetone solution gives 7.7 g (50 mmol) of TFMAA methyl ester (MTFMA) (bp 103 °C) with 70% yield. The analytical data for this product are in agreement to those reported in the literature [3].

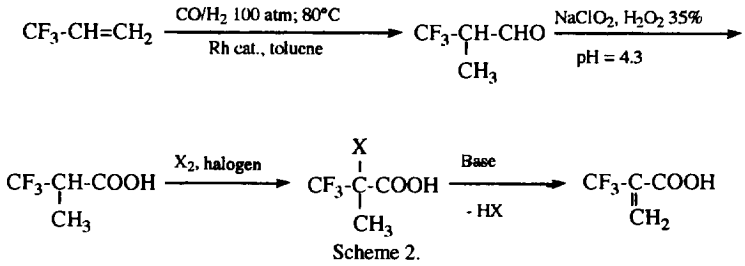
3. Results and discussion

The preparative route for MTFMA we have initially tested in our laboratory is outlined in Scheme 1.

It is known that vinyl- and other alkenyl chlorides or bromides undergo the carbonylation reaction only in the presence of a stoichiometric amount of alkylcobalt carbonyl complexes at atmospheric CO pressure in alcoholic solvent and at room temperature, affording the corresponding esters [19]. However, the use of catalysts generated in situ by interaction of $Co_2(CO)_8$ and an excess of a suitable alkyl group source (e.g. dimethylsulfate) in the basic reaction medium allows the reaction to be carried out catalytically with respect to the cobalt [14]. The first series of experiments was directed to the optimization of this reaction using the much less expensive 2-bromopropene as the substrate under different reaction conditions. From the results obtained, collected in Table 1, the following inferences can be drawn: (i) the most efficient alkylating agent used as the promoter was dimethylsulfate; (ii) the chemoselectivity of the reaction in most cases was unsatisfactory, substantial amounts of the diester, dimethyl-2-methylsuccinate, being present as a byproduct, especially at higher substrate conversion; (iii) the highest yield of methacrylate ester (> 60%) was achieved using methanol as the solvent and calcium hydroxide as the base and drastically decreasing the addition rate of the promoter to the reaction solution. Unfortunately, in several carbonylation experiments on the fluorinated isopropenyl bromide, under the above conditions, we were not able to exceed 31% yield of the desired TFMAA methyl ester (Table 1). However, the chemoselectivity in this case was > 99%, namely the catalytic process stopped, the 2-Br-TFP remaining unreacted in the reaction solution, from which it can be recovered by fractional distillation.

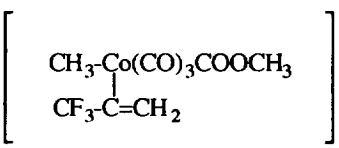


Scheme 1.



Scheme 2.

The lower activity of the fluorinated halide as compared with non-fluorinated analogue is probably due to the deactivating effect of the strongly electron-withdrawing CF_3 group towards the CO insertion reaction into a σ-alkenyl cobalt bond [20]. If the mechanism proposed for the carbonylation of aryl halides involving the intermediacy of the following octahedral complex is operative also for vinyl halides [14] the undesired CO insertion into the σlgv-methyl–cobalt bond may become competitive, as shown by the presence of a variable amount of methyl acetate in the reaction solution. Moreover, it is known that vinyl halides may somehow cause the destruction of the catalyst during the reaction [14].



We have also examined the preparative pathway to TFMAA involving the hydroformylation of TFP (Scheme 2). Recently, hydroformylation of this olefin catalyzed by $HRh(CO)(PPh_3)_3$ or other rhodium carbonyl complexes was shown to result in an almost regiospecific formation of the branched trifluoroaldehyde [15]. In a set of *oxo*-experiments carried out at 80 °C and 100 atm ($CO/H_2 = 1/1$) we reproduced the high hydroformylation yields reported in the literature (90–95%).

The subsequent oxidation of this aldehyde to the corresponding 2-(trifluoromethyl)propanoic acid (TFMPA) gave some unexpected difficulties: oxidation processes which occur under basic conditions such as Ag_2O [21] or $KMnO_4$ in acetone [22], gave only low yields of TFMPA owing to the marked tendency of the aldehyde to undergo aldol condensation; on the other hand, oxidative agents under acid conditions such as $K_2Cr_2O_7$ [23] or Caro's acid [24] cleave the substrate to lower volatile products. Good results were obtained using an aqueous solution of $NaClO_2$, H_2O_2 and NaH_2PO_4 as a buffer: yield of TFMPA up to 80% were achieved [16].

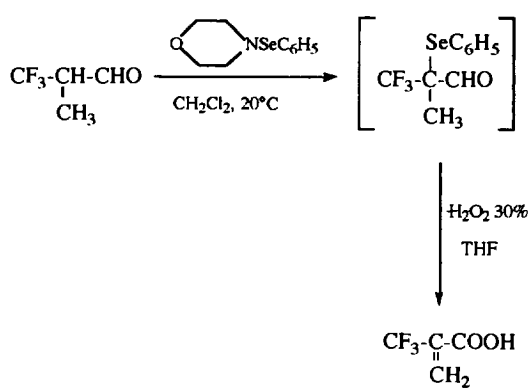
The conversion of TFMPA into TFMMA was at first attempted employing the classical two-step dehydrogenation scheme involving the α-halogenation of the saturated acid followed by dehydrohalogenation to give the desired monomer.

α-Chlorination of aliphatic acids is readily achieved using copper chloride–lithium chloride in the presence of acetyl chloride [25], sulfuryl chloride in the presence of iodine [26] or *N*-chlorosuccinimide and HCl as a catalyst [27]; α-bromination can be accomplished using bromine and phosphorus tribromide [28], *N*-bromosuccinimide and HBr as a catalyst [27] or bromine in 1,2-dichloroethane and chlorosulfonic acid as a catalyst [29]. All the aforementioned procedures failed to give appreciable yields of α-chloro or α-bromo acid or ester, when applied to TFMPA.

Very likely, the deactivation of the double bond of the enol form (usually postulated as the reactive species in the α-halogenation of carbonyl compounds [30]) caused by the presence of the strongly electron withdrawing trifluoromethyl group towards the electrophilic addition of chlorine or bromine is responsible for the disappointing results obtained in these reactions.

Finally, a straightforward preparation of TFMAA was achieved using selenium chemistry. We employed a recent very elegant route to convert saturated aldehydes to the corresponding 2-alkenoic acid via α-selenenylation with 4-(phenylseleno)morpholine formed in situ, followed by hydrogen peroxide oxidation [17].

Thus, the *oxo*-aldehyde 2-(trifluoromethyl)propanal was α-selenenylated in a one-pot reaction: a solution of the useful α-selenenylating reagent, prepared by treatment of commercially available diphenyl diselenide with bromine and morpholine [17], was allowed to interact with the fluorinated aldehyde at room temperature. The α-selenenylated derivative was not isolated but oxidized with 30% H_2O_2. This reaction brought about the formation of the corresponding selenoxide which rapidly eliminates benzeneseleninic acid giving 2-(trifluoromethyl)acrolein as an intermediate (Scheme 3). This compound underwent in turn oxidation



Scheme 3.

reaction to the desired TFMAA by the in situ formed benzenperseleninic acid: the overall yield was 73%.

TFMAA can be converted into the corresponding methylester, which is a useful monomer for polymer and co-polymer preparation [3], by reaction of its potassium salt with methyl sulphate in acetone under reflux in up to 75% yield [18]. This method proved to be more convenient than that reported by us in a previous work [3].

This preparation route is experimentally very simple but allows preparation of samples of only a few grams of TFMAA for esterification and polymerization studies.

Work is in progress to systematically investigate the carbonylation reactions on 2-Br-3,3,3-trifluoropropene and structurally related compounds to improve the chemoselectivity and the overall yield.

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