ELSEVIER

Journal of Molecular Catalysis A: Chemical 143 (1999) 287–295

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

www.elsevier.com/locate/molcata

Esters and *N,N*-dialkylamides of 2-(trifluoromethyl)acrylic acid (TFMAA) through Pd-catalysed carbonylation of fluorinated unsaturated substrates

Ugo Matteoli *, Carlo Botteghi, Federico Sbrogiò, Valentina Beghetto, Stefano Paganelli, Alberto Scrivanti

Department of Chemistry, University of Venice-Calle Larga S. Marta 2137, I-30123 Venice, Italy

Received 12 June 1998; accepted 28 August 1998

Abstract

Esters and amides of 2-(trifluoromethyl)acrylic acid (TFMAA) have been synthesised by two different routes involving CO-chemistry. The alkoxycarbonylation of 2-bromo-3,3,3-trifluoropropene was carried out in the presence of $PdCl_2(PPh_3)_2$. High substrate conversions were obtained, but the yield in acrylic esters was generally low because the desired unsaturated esters reacted further adding a molecule of alcohol to the C–C double bond. The carbonylation of 2-bromo-3,3,3-trifluoropropene in the presence of secondary amines produced the corresponding unsaturated amides in high yields; the addition of the amine to the C–C double bond also occurred, but this side reaction was minimised by using secondary cyclic amines such as morpholine or piperidine. Alternatively, the acrylic esters can be obtained by hydromethoxycarbonylation of 3,3,3-trifluoropropyne using the catalytic system $Pd(OCOCH_3)_2$/2-pyridyldiphenylphosphine/CH_3SO_3H. In this process the most important side product is the isomeric crotonic ester. The regioselectivity of the reaction can be controlled to a great extent by a suitable choice of the solvent.

Keywords: Palladium; Carbonylation; 2-(Trifluoromethyl)acrylic esters; 2-(Trifluoromethyl)acrylic amides; Acrylic monomers

1. Introduction

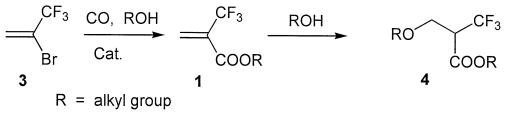
Esters of fluorinated acrylic acids are valuable starting materials for homo- and co-polymers having uncommon technological properties [1–4]. For example, we have successfully employed polyacrylates containing fluorine in their backbone as protective compounds for historical and artistic manufacts [5–7].

Our interest in preparing polyacrylates containing one or more fluorine atoms in defined positions of the repeating unit, stimulated us to set up efficient preparative routes to esters of 2-(trifluoromethyl)acrylic acid (TFMAA) of type **1** to be used for the preparation of high performance coatings [1,8].

In principle, carbonylation reactions catalysed by Pd or Co carbonyl complexes offer a convenient approach to compounds of type **1**. However, previous studies on the carbonylation of 2-bromo-3,3,3-trifluoropropene **3** in the pre-

* Corresponding author. Tel.: +39-41-2578572; Fax: +39-41-2578517; E-mail: matteol@unive.it

1381-1169/99/$ - see front matter
PII: S1381-1169(98)00396-3



Scheme 1.

sence of alcohols such as methanol and ethanol have shown that the chemoselectivity of this catalytic process is unsatisfactory, since in the best case the yield in the desired ester reaches 60% [1]. The main side product is the alkyl 2-(trifluoromethyl)-3-alkoxypropanoate **4** (Scheme 1) formed by the addition of the alcohol to the olefinic double bond of the acrylic ester **1**.

Here we report the results obtained in the synthesis of fluorinated acrylic esters of type **1** following two different preparative routes involving CO-chemistry.

Furthermore, we have synthesised some *N*,*N*-dialkylacrylamides of type **2** via carbonylation of **3** in the presence of secondary amines to test the corresponding polymeric materials as stone protectives.

2. Results and discussion

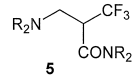
The carbonylation of the unsaturated bromide **3** was accomplished in the presence of $PdCl_2(PPh_3)_2$ as the catalytic precursor using reaction conditions close to those reported by Schoenberg and et al. [9,10] (Scheme 2).

We studied the influence of the alcohol structure in the attempt to minimise the formation of the side product **4**. Inexpensive industrially available alcohols were employed. The most representative results are reported in Table 1. The carbonylation proceeds smoothly and the substrate conversion is generally good. However, the yield in the desired ester of type **1** is generally low because of the formation of significant amounts of the by-product of type **4** and of the formation of unidentified high boiling side products. The yield in **4** exceeds that in **1** even when the bulky 2,2-dimethyl-1-propanol is employed. Using *tert*-butanol, the reactivity drastically decreases because of its steric hindrance and only traces of reaction products are detected after 160 h at 120°C and 50 atm CO.

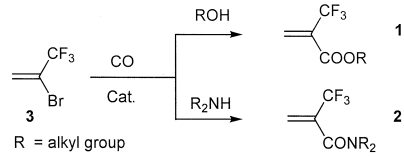
It is interesting to note that an experiment carried out under the same reaction conditions used for the carbonylations showed that **1** reacts with methanol to give **4** even in the absence of Pd(II) species. Therefore, it is conceivable that the electrophilicity of the olefinic double bond of **1** is enhanced by the strongly electron-withdrawing trifluoromethyl group which makes the unsaturation prone to undergo nucleophilic attack by the alkoxide anion.

Much more appealing results are achieved when **3** is carbonylated in the presence of secondary amines using $PdCl_2(PPh_3)_2$ as catalyst (Scheme 2). The experiments reported in Table 2 were carried out under the same conditions used in the alkoxycarbonylation reaction except for the temperature, which was increased to 120°C, because secondary amines showed to be less reactive than alcohols.

Even if prolonged reaction times are necessary to achieve high substrate conversions the yields in the unsaturated amides **2** are good because the formation of addition products of type **5** is reduced. In particular, in the presence of cyclic amines like morpholine or piperidine both the conversion (99%) and the chemoselectivity (90–94%) are excellent (Table 2, entries 5 and 6).



The steric hindrance of the amine appears to be determining in limiting the formation of **5**



Scheme 2.

Table 1
Alkoxycarbonylation of 2-bromo-3,3,3-trifluoropropene catalyzed by $PdCl_2(PPh_3)_2$

Entry	Alcohol	Time (h)	Conversion (%)[a]	**1** Yield (%)	**4** Yield (%)
1	Methanol	15	84	24	49
2	2-Propanol	66	96	36	32
3	1-Butanol	3	98	20	40
4	2-Butanol	6	93	16	38
5[b]	2,2-Dimethylpropanol	15	71	17	40

Substrate: 5.7 mmol; $PdCl_2(PPh_3)_2$: 0.1 mmol; alcohol: 7.2 mmol; tributylamine: 6.3 mmol; P(CO): 50 atm; T: 100°C.
[a] Formation of high boiling side products was observed.
[b] Tripropylamine was used.

which reaches 38% using diethylamine (Table 2, entry 2) and is negligible with diisopropylamine (Table 2, entry 4).

In the light of the disappointing results obtained in the alkoxycarbonylation of **3** we tested an alternative synthesis of the esters of TFMAA based on the hydroalkoxycarbonylation of 3,3,3-trifluoropropyne **6** (Scheme 3). This substrate is commercially available or can be conveniently prepared by (i) dehydrohalogenation with strong bases of 2-bromo-3,3,3-trifluoropropene [11], (ii) dehalogenation with Zn dust of 1,1,2-trichloro-3,3,3-trifluoropropene followed by addition of water [12].

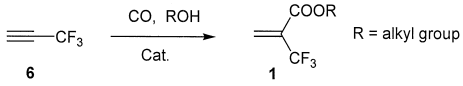
Recently, the carbonylation of alkynes has been successfully employed in the synthesis of commodities [13,14] and fine chemicals [15]. Very good results are obtained using a catalytic system formed by the combination of $Pd(OCOCH_3)_2$, 2-pyridyldiphenylphosphine and a strong organic acid like CH_3SO_3H [13,14]. This system is very active and almost completely regioselective towards the branched isomer: for example Drent reported that under mild conditions (50°C, $P(CO) = 30$ atm) propyne is hydromethoxycarbonylated with turnover numbers greater than 40.000 mol of product/(mol of Pd × hour) and selectivities to methyl methacrylate of ca. 99% [13,14].

Preliminary investigations on the carbonylation of 3,3,3-trifluoropropyne in the presence of methanol (Scheme 4) were carried out using reaction conditions close to those reported by Drent. These experiments show that the presence of the trifluoromethyl group strongly affects the catalysis: in fact, in methanol at 50°C

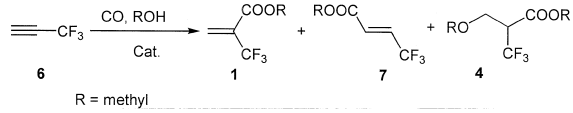
Table 2
Amidocarbonylation of 2-bromo-3,3,3-trifluoropropene catalyzed by $PdCl_2(PPh_3)_2$

Entry	Amine	Time (h)	Conversion (%)	**2** Yield (%)	**5** Yield (%)
1	Diethylamine	22	67[a]	25	15
2[b,c]	Diethylamine	22	99[a]	57	38
3[d]	Diisopropylamine	90	99[a]	75	20
4[e]	Diisopropylamine	90	85[a]	70	-
5[b,c]	Morfoline	45	99	94	5
6[b,c]	Piperidine	45	99	90	9

Substrate: 5.7 mmol; $PdCl_2(PPh_3)_2$: 0.1 mmol; P(CO): 50 atm; T: 120°C; amine: 6.3 mmol.
[a] Formation of high boiling side products was observed.
[b] 5.7 mmol of triethylamine were also added as HBr scavenger.
[c] Tetrahydrofuran (5 ml) was added as solvent.
[d] Amine: 26.8 mmol.
[e] Amine: 17.1 mmol.



Scheme 3.



Scheme 4.

(Table 3, entry 1) the carbonylation of 3,3,3-trifluoropropyne requires long reaction times and both **1** and **7** are formed in ca. 1.2 molar ratio. Traces of **4** are also formed.

The influence of the nature of the solvent, the temperature, and $P(CO)$ on the chemoselectivity of the reaction has been investigated in order to maximise the yield in acrylic ester. The most representative results are collected in Table 3.

It appears that the solvent plays the most important role affecting both the rate and the regioselectivity of the reaction. In particular, the use of *N*-methylpyrrolidone (NMP) [14] enhances the regioselectivity towards the acrylic ester albeit the reaction rate is reduced. We tested solvent mixtures containing little amounts of NMP in order to reach a good compromise between the good reaction rate obtained in methanol and the high regioselectivity obtained in NMP. Accordingly, the use of a 9/1 methanol/NMP mixture (Table 3, entry 3) produces a substantial enhancement of the **1**/**7** ratio even if a modest decrease in the reaction rate with the respect to the use of neat methanol is observed. Better results are obtained using dichloromethane/NMP mixtures: in particular, using a 9/1 mixture the regioselectivity goes up to 3.0 (Table 3, entry 4). Using a 1/1 dichloromethane/NMP mixture the **1**/**7** ratio increases up to ca. 13, but the catalytic activity becomes exceedingly low.

The results obtained in the carbonylation of **6** are consistent with the reaction mechanism we have recently proposed [16]. As a matter of fact, our investigations indicated that the key step of the catalytic cycle involves the formation of a Pd–vinyl intermediate by protonation of an alkyne-Pd species (Scheme 5).

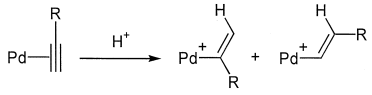
Accordingly, the low carbonylation rate of **6** is attributable to the presence of the strong electro-withdrawing trifluoromethyl group, which makes the adjacent carbon atom less susceptible of attack by an electrophilic reagent. This effect can also account for the low regioselectivity obtained in the carbonylation of **6**. It is rather difficult to provide a reasonable explanation for the effect played by NMP, however it should be noted that this solvent has a basic behaviour [17] which may influence both the reactivity of the proton and the coordination sphere of the palladium.

The use of a fluorinated solvent such as 1,1,2-trichlorotrifluoroethane (Table 3) does not allow to obtain substantial improvements in the regioselectivity. As with the other solvents the

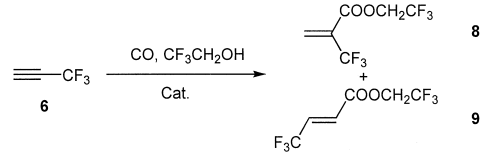
Table 3
Hydroalkoxycarbonylation of 3,3,3-trifluoropropyne in the presence of methanol: effect of the solvent

Entry	Solvent	Time (h)	Conversion (%)	**1** Yield (%)	**7** Yield (%)	**1**/**7**
1	CH_3OH	24	85	47	38	1.2
2	NMP	24	3.5	3.1	0.4	7.8
3	CH_3OH/NMP (9/1)	24	60	39	21	1.9
4	CH_2Cl_2/NMP (9/1)	24	52	39	13	3.0
5	CH_2Cl_2/NMP (1/1)	46	55	51	4	12.8
6[a]	Cl_2FCCF_2Cl	20	49	32	17	1.9
7[a]	Cl_2FCCF_2Cl/NMP (9/1)	20	12	10	2	5.0

Substrate: 12.0 mmol; CH_3OH: 42.0 mmol; solvent: 20 ml; $Pd(OCOCH_3)_2$: 0.025 mmol; $PyPPh_2$: 1 mmol; CH_3SO_3H: 1 mmol; $P(CO)$: 40 atm; T: 50°C.
[a] $P(CO)$: 80 atm.



Scheme 5.



Scheme 6.

addition of a small amount of NMP provides an enhancement of the regioselectivity at the expense of the catalytic activity.

In Table 4 are reported the data obtained using different reaction temperatures: it appears that the best results are achieved carrying out the reaction at 80°C, since at higher temperatures both the regioselectivity and the reaction rate decrease. This fact may probably be attributed to a partial decomposition of the catalyst and/or to a decrease of concentration of the substrate in solution owing to the higher temperature.

The hydroalkoxycarbonylation of fluoroalkynes can be conveniently used to synthesise esters of TFMAA having fluorine atoms in the ester moiety. For example the carbonylation of **6** in the presence of 2,2,2-trifluoroethanol (Scheme 6) affords the corresponding acrylic ester in good yield (Table 5).

When the reaction is carried out in neat trifluoroethanol, the acrylic **8** and crotonic **9** esters are formed in almost 1/1 ratio (entry 1). Using 1,1,2-trichlorotrifluoroethane as solvent the reaction rate is enhanced but the **8**/**9** ratio becomes 0.3 (entry 2). Also in this case, the formation of the branched isomer is favoured by the use of NMP in mixture with other solvents: in fact, as found with methanol, the presence of NMP strongly enhances the formation of the acrylic ester even if the reaction rate decreases (entries 3 and 4).

3. Concluding remarks

The obtained results indicate that for the synthesis of TMFAA esters the hydroalkoxycarbonylation of 3,3,3-trifluoropropyne is more suitable than the alkoxycarbonylation of 2-bromo-3,3,3-trifluoropropene. As a matter of fact the alkyne based route offers a greater chemoselectivity likely owing to the acidic character of the reaction medium. At variance of that found in the case of non-fluorinated aliphatic alkynes the regioselectivity of the reaction is not complete. However, our investigations demonstrate that the regioselectivity may be controlled to a great extent by a careful optimisation of the reaction parameters. From a synthetic point of view the possibility to obtain the crotonic or the methacrylic ester by a suitable tuning of the reaction conditions seems very useful.

Moreover, the alkyne-based route allows to obtain a straightforward synthesis of methacrylic monomers containing fluorine atoms both on the methyl group and on the ester moiety. Interesting results have also been obtained in the

Table 4
Hydroalkoxycarbonylation of 3,3,3-trifluoropropyne in the presence of methanol: effect of the temperature

T (°C)	Solvent	Conversion (%)	**1** Yield (%)	**7** Yield (%)	**1**/**7**
50	CH_2Cl_2/NMP (9/1)	52	39	13	3.0
80	CH_2Cl_2/NMP (9/1)	100	73	27	2.7
120	CH_2Cl_2/NMP (9/1)	93	51	42	1.2

Substrate: 12.0 mmol; CH_3OH: 42.0 mmol; solvent: 20 ml; $Pd(OCOCH_3)_2$: 0.025 mmol; $PyPPh_2$: 1 mmol; CH_3SO_3H: 1 mmol; *P*(CO): 40 atm; reaction time: 24 h.

Table 5
Hydroalkoxycarbonylation of 3,3,3-trifluoropropyne in the presence of 2,2,2-trifluoroethanol

Entry	Solvent	Time (h)	Conversion (%)	**8** Yield (%)	**9** Yield (%)	**8**/**9**
1	CF_3CH_2OH	24	26	13	13	1.0
2	Cl_2FCCF_2Cl	24	50	11	39	0.3
3	Cl_2FCCF_2Cl/NMP (39/1)	94	83	34	49	0.7
4	Cl_2FCCF_2Cl/NMP (9/1)	90	23	20	3	6.7

Substrate: 12.0 mmol; CF_3CH_2OH: 42.0 mmol; solvent: 20 ml; $Pd(OCOCH_3)_2$: 0.025 mmol; $PyPPh_2$: 1 mmol; CH_3SO_3H: 1 mmol; *P*(CO): 80 atm; *T*: 50°C.

synthesis of *N,N*-dialkylmethacrylamides via alkoxycarbonylation of 2-bromo-3,3,3-trifluoropropene. In particular, good results have been obtained using bulky secondary amines or cyclic amines such as piperidine.

Further studies are in progress to synthesise fluorinated methacrylamides by the alkyne based route.

4. Experimental

All the operations were carried out under argon in Schlenk-type glassware. Alcohols, amines,2-pyridyldiphenylphosphine and methanesulfonic acid were commercial products (Aldrich). Solvents (C. Erba) were purified following methods described in literature [18]. $Pd(OCOCH_3)_2$ was purchased from Engelhard. $PdCl_2(PPh_3)_2$ was prepared as described in literature [19]. 3,3,3-Trifluoropropyne and 2-bromo-3,3,3-trifluoropropene were commercial products (Fluorochem).

Carbonylation experiments were carried out in a magnetically stirred stainless steel autoclave (total volume ca. 150 ml). Conversions and yields of the carbonylation reactions were determined by GLC on a Hewlett-Packard 5890 II series gaschromatograph using *p*-xylene as internal standard. The products were characterised by GLC-MS using a HP 5890 II series gaschromatograph interfaced to a Hewlett-Packard 5971 mass detector. Some of the products were also characterised by ^{1}H-NMR spectroscopy using a Bruker AC 200 spectrometer operating at 200.13 MHz.

4.1. Carbonylation of 2-bromo-3,3,3-trifluoropropene

In a typical experiment (run 2 of Table 2) the autoclave was charged with 1 g (5.7 mmol) of 2-bromo-3,3,3-trifluoropropene, 460 mg (6.3 mmol) of diethylamine, 575 mg (5.7 mmol) of triethylamine, 70 mg (0.1 mmol) of $PdCl_2(PPh_3)_2$ and 5 ml of tetrahydrofurane. The reactor was then pressurised with carbon monoxide (50 atm). The vessel was heated at 120°C ($\pm$1°C) by circulating a thermostatic fluid. After 22 h the residual gas was vented off, the raw reaction mixture was purified by flash chromatography (silica gel, hexane/diethylether) and the products identified by ^{1}H-NMR spectroscopy and GC-MS.

4.2. Carbonylation of 3,3,3-trifluoropropyne

The experimental details for run 1 of Table 3 are reported. Under inert atmosphere a Schlenk flask containing a small magnetic bar is charged with 263 mg (1.0 mmol) of 2-pyridyldiphenylphosphine, 5.6 mg (0.025 mmol) of $Pd(OCOCH_3)_2$, 20 ml of methanol and 96 mg (1.0 mmol) of CH_3SO_3H. The resulting solution is transferred via cannula into the autoclave. The reactor is charged with 1.0 g (12 mmol) of 3,3,3-trifluoropropyne, then pressurised with CO (40 atm). The reactor was heated at 50°C ($\pm$1°C) by circulating a thermostatic fluid. After 24 h the residual gas was vented off and the composition of the raw reaction mixture determined by GLC.

4.3. Characterisation of products

4.3.1. n-Butyl 2-(trifluoromethyl)acrylate

MS (m/e): 195 ($M^+ - 1$); 167 (M^+–CH_2CH_3); 123 ($CH_2=CCF_3CO^+$); 101 ($COO(CH_2)_3CH_3^+$); 95 ($CH_2=CCF_3^+$); 75 ($CF_2=C=CH^+$); 69 (CF_3^+); 41 ($CH_2=CHCH_2^+$).

4.3.2. n-Butyl 2-(trifluoromethyl)-3-(n-butoxy)-propanoate

MS (m/e): 270 (M^+); 227 (M^+–$CH_2CH_2CH_3$); 171 (M^+–($CH_3CH=CH_2$)–(C_4H_9)); 141 (M^+–($O(CH_2)_3CH_3$)–(C_4H_8)); 87 ($CH_3(CH_2)_3OCH_2^+$); 73 ($O(CH_2)_3CH_3^+$); 57 ($CH_3(CH_2)_3^+$); 41 ($CH_2=CHCH_2^+$); 29 ($CH_3CH_2^+$).

4.3.3. s-Butyl 2-(trifluoromethyl)acrylate

MS (m/e): 195 ($M^+ - 1$); 181 (M^+–CH_3); 167 (M^+–CH_2CH_3); 123 ($CH_2=CCF_3CO^+$); 101 ($COOCH_2CH(CH_3)_2^+$); 95 ($CH_2=CCF_3^+$); 75 ($CF_2=C=CH^+$); 69 (CF_3^+); 41 ($CH_2=CHCH_2^+$).

4.3.4. s-Butyl 2-(trifluoromethyl)-3-(s-butoxy)-propanoate

MS (m/e): 255 (M^+–CH_3); 241 (M^+–CH_2CH_3); 213 (M^+–$CH_2CH(CH_3)_2$); 197 (M^+–$OCH_2CH(CH_3)_2$); 123 ($CH_2=CCF_3CO^+$); 87 ($(CH_3)_2CHCH_2OCH_2^+$); 73 ($OCH_2CH(CH_3)_2^+$); 69 (CF_3^+); 43 ($CH_3CH_2CH_2^+$); 29 ($CH_3CH_2^+$).

4.3.5. t-Butyl 2-(trifluoromethyl)acrylate

MS (m/e): 181 (M^+–CH_3); 123 ($CH_2=CCF_3CO^+$); 95 ($CH_2=CCF_3^+$); 75 ($CF_2=C=CH^+$); 69 (CF_3^+); 57 ($(CH_3)_3C^+$); 15 (CH_3^+).

4.3.6. Isopropyl 2-(trifluoromethyl)acrylate

MS (m/e): 181 ($M^+ - 1$); 167 (M^+–CH_3); 123 ($CH_2=CCF_3CO^+$); 95 ($CH_2=CCF_3^+$); 75 ($CF_2=C=CH^+$); 69 (CF_3^+); 57 ($CH_2=CCH_3O^+$); 43 ($(CH_3)_2CH^+$).

4.3.7. Isopropyl 2-(trifluoromethyl)-3-(isopropoxy)propanoate

MS (m/e): 241 ($M^+ - 1$); 213 (M^+–CH_2CH_3); 199 (M^+–$CH(CH_3)_2$); 95 ($CH_2=CCF_3^+$); 87 ($COOCH(CH_3)_2^+$); 73 ($CH_2OCH(CH_3)_2^+$); 69 (CF_3^+); 59 ($OCH(CH_3)_2^+$); 57 ($CH_2=CCH_3O^+$); 43 ($(CH_3)_2CH^+$).

4.3.8. 2,2-Dimethylpropyl 2-(trifluoromethyl)-acrylate

MS (m/e): 195 (M^+–CH_3); 123 ($CH_2=CCF_3CO^+$); 115 ($COOCH_2C(CH_3)_3^+$); 95 ($CH_2=CCF_3^+$); 75 ($CF_2=C=CH^+$); 69 (CF_3^+); 57 ($(CH_3)_3C^+$); 41 ($CH_2=CCH_3^+$).

4.3.9. 2,2-Dimethylpropyl 2-(trifluoromethyl)-3-(2,2-dimethylpropoxy)propanoate

MS (m/e): 283 (M^+–CH_3); 241 (M^+–$C(CH_3)_3$); 227 (M^+–$CH_2C(CH_3)_3$); 123 ($CH_2=CCF_3CO^+$); 95 ($CH_2=CCF_3^+$); 87 ($OCH_2C(CH_3)_3^+$); 71 ($CH_2C(CH_3)_3^+$); 69 (CF_3^+); 57 ($(CH_3)_3C^+$); 41 ($CH_2=CCH_3^+$).

4.3.10. Methyl 2-(trifluoromethyl)acrylate

^{1}H-NMR ($CDCl_3$, ppm): 3.75 (s, 3H), 6.33 (m, 1H), 6.59 (m, 1H). MS (m/e): 154 (M^+); 135 ($CH_2=C=CF_2COOCH_3^+$); 123 ($CH_2=CCF_3CO^+$); 95 ($CH_2=CCF_3^+$); 75 ($CF_2=C=CH^+$); 69 (CF_3^+); 59 ($COOCH_3^+$); 31 (OCH_3^+); 15 (CH_3^+).

4.3.11. Methyl 2-(trifluoromethyl)-3 methoxy-propanoate

MS (m/e): 186 (M^+); 171 (M^+–CH_3); 155 (M^+–OCH_3); 127 (M^+–$COOCH_3$); 117 (M^+–CF_3); 85 ($CH_2=CCOOCH_3^+$); 69 (CF_3^+); 59 ($COOCH_3^+$); 45 ($CH_3OCH_2^+$); 31 (OCH_3^+); 15 (CH_3^+).

4.3.12. Methyl 4,4,4-trifluorocrotonate

^{1}H-NMR ($CDCl_3$, ppm): 3.65 (s, 3H), 6.37 (m, 1H), 6.69 (m, 1H). MS (m/e): 135 ($CF_2CH=CHCOOCH_3^+$); 123 ($CH_2=CCF_3CO^+$); 95 ($CH_2=CCF_3^+$); 85

($CH{=}CHCOOCH_3^+$); 75 ($CF_2{=}C{=}CH^+$); 69 (CF_3^+).

4.3.13. N,N-Diethyl 2-(trifluoromethyl)-acrylamide

^{1}H-NMR ($CDCl_3$, ppm): 1.08–1.25 (m, 6H), 3.25–3.60 (m, 4H), 5.63 (s, 1H), 5.95 (s, 1H). MS (*m/e*): 195 (M^+); 180 (M^+–CH_3); 166 (M^+–CH_2CH_3); 123 ($CH_2{=}CCF_3CO^+$); 95 ($CH_2{=}CCF_3^+$); 69 (CF_3^+); 29 ($CH_2CH_3^+$); 15 (CH_3^+).

4.3.14. N,N-Diisopropyl 2-(trifluoromethyl)-acrylamide

^{1}H-NMR ($CDCl_3$, ppm): 1.00–1.32 (m, 6H), 1.32–1.70 (m, 6H), 3.25–3.65 (m, 1H), 3.85–4.25 (m, 1H), 5.55 (s, 1H), 5.90 (s, 1H). MS (*m/e*): 223 (M^+); 208 (M^+–CH_3); 180 (M^+–$CH(CH_3)_2$); 166 (M^+–($CH_2{=}CHCH_3$)–(CH_3)); 123 ($CH_2{=}CCF_3CO^+$); 100 ($N(CH(CH_3)_2)_2^+$); 95 ($CH_2{=}CCF_3^+$); 69 (CF_3^+); 15 (CH_3^+).

4.3.15. N[(2-Trifluoromethyl)-acryloyl]piperidine

^{1}H-NMR ($CDCl_3$, ppm): 1.30–1.80 (m, 6H), 3.30–3.80 (m, 4H), 5.65 (s, 1H), 6.02 (s, 1H). MS (*m/e*): 207 (M^+); 206 (M^+-1); 186 (206^+–HF); 178 (M^+–C_2H_5); 164 (M^+–C_3H_7); 150 (M^+–C_4H_9); 138 (M^+–CF_3); 123 ($CH_2{=}CCF_3CO^+$); 95 ($CH_2{=}CCF_3^+$); 84 ($N(CH_2)_5^+$); 69 (CF_3^+); 56 ($C_4H_8^+$); 55 ($C_4H_7^+$); 42 ($C_3H_6^+$); 41 ($C_3H_5^+$); 29 ($C_2H_5^+$).

4.3.16. N[(2-Trifluoromethyl)acryloyl]-morpholine

^{1}H-NMR ($CDCl_3$, ppm): 3.40–3.90 (m, 8H), 5.70 (s, 1H), 6.10 (s, 1H). MS (*m/e*): 209 (M^+); 208 (M^+-1); 194 (M^+–CH_3); 190 (M^+–F); 188 (208^+–HF); 180 (M^+–C_2H_5); 178 (M^+–OCH_3); 164 (M^+–OC_2H_5); 159 (190^+–OCH_3); 150 (M^+–OC_3H_7); 140 (M^+–CF_3); 136 (M^+–OC_4H_9); 123 ($CH_2{=}CCF_3CO^+$); 114 ($CON(CH_2)_2O(CH_2)_2^+$); 95 ($CH_2{=}CCF_3^+$); 86 ($N(CH_2)_2O(CH_2)_2^+$); 69 (CF_3^+); 56 ($C_3H_6N^+$); 42 ($C_2H_4N^+$); 29 ($C_2H_5^+$).

4.3.17. N,N-Diethyl 2-(trifluoromethyl)-3-(N,N-diethylamino)propanamide

^{1}H-NMR ($CDCl_3$, ppm): 0.90-1.05 (t, 6H), 1.05–1.18 (t, 3H), 1.18–1.32 (t, 3H), 2.32-2.62 (m, 4H), 2.68–2.80 (dd, 1H), 3.12–3.30 (dd, 1H), 3.30–3.60 (m, 5H). MS (*m/e*): 268 (M^+); 253 (M^+–CH_3); 239 (M^+–CH_2CH_3); 196 (M^+–$N(CH_2CH_3)_2$); 168 (M^+-$CON(CH_2CH_3)_2$); 148 (168^+–HF); 123 ($CH_2{=}CCF_3CO^+$); 100 ($CON(CH_2CH_3)_2^+$); 86 ($CH_2N(CH_2CH_3)_2^+$); 72 ($N(CH_2CH_3)_2^+$); 69 (CF_3^+); 56 ($C_2H_2NO^+$); 42 ($C_2H_4N^+$); 29 ($C_2H_5^+$); 15 (CH_3^+).

4.3.18. N,N-Diisopropyl 2-(trifluoromethyl)-3-(N,N-diisopropylamino)propanamide

^{1}H-NMR ($CDCl_3$, ppm): 0.97 (d, 12H), 1.18–1.25 (dd, 6H), 1.35–1.44 (dd, 6H), 2.73–2.83 (dd, 1H), 2.84–3.10 (m, 2H), 3.19–3.33 (dd, 1H), 3.38–3.59 (m, 2H), 4.00–4.23 (m, 1H). MS (*m/e*): 309 (M^+–CH_3); 281 (M^+–$CH(CH_3)_2$); 224 (M^+–$N(CH(CH_3)_2)_2$); 166 (309^+–($N(CH(CH_3)_2)_2$)–($CH(CH_3)_2$)); 154 (M^+–($CON(CH(CH_3)_2)_2$)–($CH_3CH{=}CH_2$)); 140 (224^+–(CF_3)–(CH_3)); 128 (CO^+); 114 ($CH_2N(CH(CH_3)_2)_2^+$); 98 (($CH_3C{=}CH_2$)$N(CH(CH_3)_2)_2^+$); 86 (114^+–C_2H_4); 69 (CF_3^+); 56 ($C_3H_6N^+$); 43 (C_3H_7); 15 (CH_3^+).

4.3.19. [2-Trifluoromethyl-3-(1-piperidino)-propanoyl]piperidine

^{1}H-NMR ($CDCl_3$, ppm): 1.45–1.80 (m, 12H), 2.25–2.52 (m, 1H), 2.58–2.72 (dd, 1H), 3.08–3.21 (dd, 1H), 3.38–3.85 (m, 8H). MS (*m/e*): 292 (M^+); 263 (M^+–C_2H_5); 223 (M^+–CF_3); 208 (M^+–$N(CH_2)_5$); 180 (M^+–$CON(CH_2)_5$); 166 (180^+–CH_2); 152 (180^+–C_2H_4); 138 (180^+–C_3H_6); 123 ($CH_2{=}CCF_3CO^+$); 98 ($CH_2N(CH_2)_5^+$); 84 ($N(CH_2)_5^+$); 69 (CF_3^+); 55 ($C_4H_7^+$); 41 ($C_3H_5^+$).

4.3.20. [2-Trifluoromethyl-3-(1-morpholino)-propanoyl]morpholine

^{1}H-NMR ($CDCl_3$, ppm): 2.40–2.60 (m, 1H), 2.62–2.78 (dd, 1H), 3.12–3.30 (dd, 1H), 3.35–3.90 (m, 16H). MS (*m/e*): 296 (M^+); 227

(M^+–CF_3); 210 (M^+–$N(CH_2)_2O(CH_2)_2$); 196 (M^+–$CH_2N(CH_2)_2O(CH_2)_2$); 86 ($N(CH_2)_2O(CH_2)_2^+$); 69 (CF_3^+).

Acknowledgements

This work was supported by the Italian C.N.R. Progetto Finalizzato 'Beni Culturali'.

References

[1] M. Aglietto, E. Passaglia, L. Montagnini di Mirabello, C. Botteghi, S. Paganelli, U. Matteoli, G. Menchi, Macromol. Chem. Phys. 196 (1995) 2843.
[2] L.S. Boguslavskaya, I.Yu. Panteleeva, T.V. Morozova, A.V. Kartashov, N.N. Chuvatkin, Russian Chem. Rev. 59 (1990) 906.
[3] D. Sianesi, Chim. Ind. (Milan) 79 (1997) 333.
[4] W. Graham, European Coatings J. (1997) 494.
[5] C. Botteghi, U. Matteoli, S. Paganelli, R. Arbizzani, F. Ciardelli, M. Aglietto, E. Taburoni, V. Fassina, Science and Technology for Cultural Heritage 1 (1992) 111.
[6] M. Aglietto, E. Passaglia, E. Taburoni, F. Ciardelli, C. Botteghi, U. Matteoli, S. Paganelli, R. Arbizzani, V. Fassina, ICOM, Committee for Conservation, 10th Triennial Meeting, Washington, 22–27 Agosto 1993, pp. 553–558.
[7] V. Fassina, R. Arbizzani, C. Botteghi, U. Matteoli, E. Passaglia, M. Aglietto, Proceedings 3rd International Symposium on The Conservation of Monuments in the Mediterranean Basin, Venezia, 22–25 giugno 1994, pp. 911–918.
[8] C. Botteghi, C. Lando, U. Matteoli, S. Paganelli, G. Menchi, J. Fluorine Chem. 83 (1997) 67.
[9] A. Schoenberg, R.F. Heck, J. Org. Chem. 39 (1974) 3327.
[10] A. Schoenberg, I. Bartoletti, R.F. Heck, J. Org. Chem. 39 (1974) 3318.
[11] A.L. Henne, M. Nager, J. Am. Chem. Soc. 73 (1951) 1042.
[12] W.G. Finnegan, W.P. Norris, J. Org. Chem. 28 (1963) 1139.
[13] E. Drent, P. Arnoldy, P.H.M. Budzelaar, J. Organometal. Chem. 455 (1993) 247.
[14] E. Drent, P. Arnoldy, P.H.M. Budzelaar, J. Organometal. Chem. 475 (1994) 57.
[15] A. Scrivanti, U. Matteoli, Tetrahedron Lett. 36 (1995) 9015.
[16] A. Scrivanti, V. Beghetto, E. Campagna, M. Zanato, U. Matteoli, Organometallics 17 (1998) 630.
[17] R.L. Adelman, J. Org. Chem. 29 (1964) 1837.
[18] W.L.F. Armarego, D.D. Perrin, Purification of Laboratory Chemicals, Butterworth-Heinemann, IV edn., Oxford, 1996.
[19] J. Chatt, L.M. Venanzi, J. Chem. Soc. (1957) 2352.