Tetrahedron Letters 54 (2013) 6271–6274

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Synthesis of fluorinated malonamides and use in L/L extraction of *f*-elements

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ARTICLE INFO

Article history:
Received 18 January 2013
Revised 9 September 2013
Accepted 11 September 2013
Available online 18 September 2013

Keywords:
Fluorinated compounds
Solvent extraction
f-Elements
Malonamide extractants
Lanthanides

ABSTRACT

Synthesis of new fluorinated tertiary malonamides (F-malonamides) was accomplished, and their liquid/liquid (L/L) extraction properties with *f*-elements were investigated. These molecules are fluorinated analogues of well known extractants used in several processes designed towards the treatment of nuclear wastes, and the efficient separation of lanthanides from minor actinides; however, the synthesis of F-malonamides deserved a modification of the general synthetic route commonly employed to prepare H-malonamides. Extraction of neodymium from various aqueous media into both fluorous and classical solvents was studied, which revealed an opposite trend between F-malonamides and H-malonamides: L/L extraction ability is very sensitive to the nitrogen atoms substitution pattern, and the most efficient F-malonamide is compound **3** (R_1 = Me), whereas the best H-malonamide is compound **5** (R_1 = Bu, DMDBTDMA).

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Introduction

Recovery of *f*-elements is a research subject of fast growing importance, with the need for efficient recycling of several rare earth metals, commonly used in optical, electronic, and magnetic devices.[1] Amongst the different envisioned processes, hydrometallurgical ones are promising, since they are already well mastered for (1) pure rare earth production from different natural ores,[2] and (2) partitioning of nuclear fuel fission products.[3] In both cases, after digestion of solid matter with an acidic solution (hydrochloric, sulfuric or nitric), the metal cations are isolated from organic phases after the liquid/liquid (L/L) extraction.[4] Efficient extracting systems, based on amphiphilic molecules, were developed, but each system remains devoted to a particular input feed, with limited balance between constituents in the aqueous layer. As a remarkable example, whereas HDEHP (di-2-ethylhexylphosphoric acid) used alone in a L/L extraction process enables efficient purification of heavy lanthanides, separation factors are too low to purify light lanthanides and actinides mixtures with this sole molecule.[5] All these metals present at the +III oxidation state, are hard cations, and differ only in their radii, as revealed by the lanthanide contraction.[6]

Malonamide ligands, with general formula $(MeR_1NCO)_2CHR$, are neutral amphiphilic molecules which have proved their potency for the extraction of *f*-elements since the early 60 s.[7] Later on, several structural modifications led to the development of efficient processes for the retreatment of nuclear wastes, aimed at the lanthanide-actinide separation.[8] The introduction of various long hydrocarbon chains enables fine tuning of the hydrophobic properties of the molecules, responsible for the structuration of the organic layer, one of the key parameters for selective and efficient L/L extraction.[9] The ability to coordinate metal ions, and especially *f*-elements, results from the thermodynamic stabilization induced by the chelate effect of the bidentate coordination mode. The best candidate molecules today are the *N*,*N*′-tetrasubstituted-2-alkylated malonamides DMDBTDMA ($R_1 = n\text{-}C_4H_9$ and $R = n\text{-}C_{14}H_{29}$) and DMDOHEMA ($R_1 = n\text{-}C_8H_{17}$ and $R = n\text{-}C_2H_4OC_6H_{13}$) depicted in Figure 1.[10] They were developed to ameliorate the HDEHP extraction, and take profit of the fact that actinides(III) such as Am and Cm are a little softer than their lanthanide counterparts, with a larger 5*f* orbital enabling *f*-electrons to participate in the chemical bonding.[11] They represent today the benchmark in *f*-elements L/L extraction, and are also used in other separation techniques e.g., extraction chromatography,[12] or hybrid functional materials for solid–liquid extraction such as silica[13] and magnetic particles.[14]

Interestingly, as fluorous chemistry[15] proved its efficiency in various fields including L/L extraction and purification of organic and inorganic compounds,[16] to our knowledge only one publication deals with the adaptation of this technology for the separation of *f*-elements, employing a polypyridine chelating agent,[17] and even very few with the extraction of *d*-elements.[18] Interests of fluorous techniques are multiple: extraction kinetics may be

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http://dx.doi.org/10.1016/j.tetlet.2013.09.031

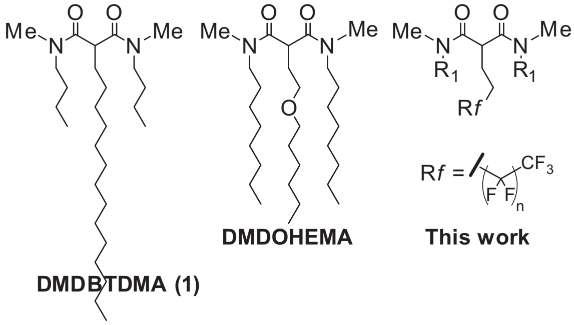


Figure 1. Classical malonamide extractants used for the selective separation of *f*-elements: *N*,*N*′-dimethyl-*N*,*N*′-dibutyl-2-tetradecyl malonamide (**DMDBTDMA**, **1**); *N*-*N*′-dimethyl-*N*,*N*′-dioctyl-2-hexaethyl malonamide (**DMDOHEMA**); and targeted fluorinated malonamides.

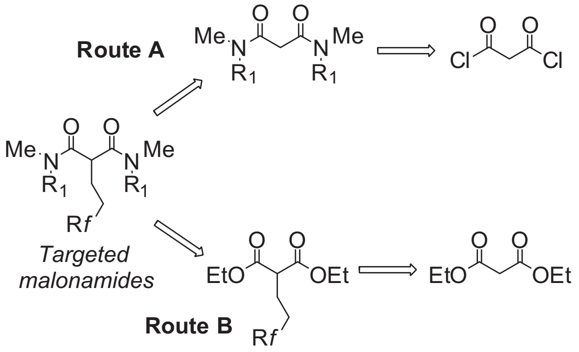
improved, as dynamic surface tension measurements proved a better affinity of F-surfactants for interfaces.[19] Also, the chemical stability of the C–F bond makes F-organic derivatives very stable, including towards radiation.[20] Then, as F-compounds are much less soluble in water than their H-analogues, leaching of the extracting molecule into the aqueous layer should be lower. Finally, '3-phases' (aqueous/organic/fluorous) system and temperature dependent phase separation are possible and offer more opportunities in L/L extraction.[21]

It is the purpose of this Letter to report the preparation of fluorinated malonamides (F-malonamides), directly inspired from DMDBTDMA (**1**, Fig. 1), and our first results regarding the issues related to L/L extraction with these compounds.

Synthesis

The synthesis of all malonamides employed for nuclear waste treatments relies on the monoalkylation of the activated methylene of suitable *N*,*N*′-tetrasubstituted malonamides (Route A, Scheme 1). As the *N*-substituents become bulkier, yields of the alkylation drop severely. And then, as the final products are oily compounds which tend to drag on silica gel during purification with flash chromatography, they become difficult to obtain in decent yield and purity, especially on a large scale.[22]

When adapting this classical route to perfluorinated alkylating agents, such as 1*H*,1*H*,2*H*,2*H*-perfluorooctyl iodide, it was only possible to obtain the target compound **3** starting from *N*,*N*′-tetramethyl malonamide **2**, thanks to the low steric effect on the amide groups, albeit with a poor yield (12%, Scheme 2). All other substitution patterns resulted in the desired compound in trace amount only.



Scheme 1. Envisioned synthesis of hydrocarbonated and fluorinated malonamide-based extractants: Route A starting from malonyl chloride, Route B from diethylmalonate.

Thus, the amide-formation step and the alkylation had to be inverted (Route B, Scheme 1). To our knowledge, this route was only used for the preparation of secondary malonamides, where N-alkylation is expected when following Route A.[23] Required substituted diethyl malonates **7**–**9** were obtained according to a reported procedure:[24] starting from diethyl malonate which possesses an enhanced reactive methylene compared to tertiary malonamides, monoalkylation with various alkyl bromides or iodides, including perfluoroalkyl iodides, is very efficient, with yields higher than 80% after purification with bulb-to-bulb distillation on a multigram scale. Then, direct di-amide formation from these di-esters and the corresponding secondary amine was attempted in the case of ester **7**, but only selective decarboxylation and formation of the mono-amide **10** were observed (Scheme 2). Use of Lewis acids such as $BF_3{\cdot}OEt_2$ did not change the outcome of this reaction.

The only efficient way to obtain the desired substituted F-malonamides consisted in (1) hydrolysing the di-ester into the corresponding di-acid, and (2) activating it into the di-acid chloride, then reacting the latter in situ with the suitable amine (Scheme 2). The first step does not deserve any other purification than extraction from aqueous layer, and drying in vacuo,[†] so that only one final purification with chromatography on silica gel is necessary, as already performed on large scale with Route A (see Ref. 22). Thus, the desired F-malonamides were synthesized with yields ranging from 55 to 70% from di-esters **7**–**9**, depending on the chosen amine (bulky secondary amines leading to lower yields), and the F-chain (Scheme 2 and Table 1).[25]

These compounds are either waxy solids or oils. Although they clearly show supramolecular organization (birefringent behaviour during observation under polarized light optical microscope), their differential thermal analysis (DTA) curves do not show other transition than melting/solidification. When R_1 is a butyl group, the ^1H and ^{13}C NMR spectra exhibits up to four sets of signals which are characteristic of *ZZ*, *EZ* and *EE* isomers due to the *cis*/*trans* conformations of the tertiary amide bonds, as previously observed in the hydrocarbonated compound **1**.[26] Thus, in $CDCl_3$, the ^1H NMR spectra of compounds **5**, **15** and **17** reveal four singlets for the N-CH_3 signal, and complicate multiplets for some other signals. In the ^{13}C NMR spectra, four distinct different peaks appear for the C=O, NCH_3 and NH_2 signals. Even the methyl group at the end of the butyl chain leads to several signals with different chemical shifts in both types of spectra. ^1H NMR analysis of compound **5** was also performed in toluene-d8: at 298 K, a clear separation of each triplet characteristic of the malonic proton is obtained, and heating to 378 K leads to a clean transition into a unique signal for this proton, as well as a clean whole spectrum, guarantee of the purity of the prepared compound (see Supplementary data). These isomers are not found in symmetrical compounds **3**, **14** and **16** where R_1 = Me.

Liquid/liquid extraction

Our first surprise was the poor solubility of prepared F-malonamides in common fluorinated solvents such as perfluorohexane or perfluorotoluene. Solubility tests proved that compounds **5**, **15** and **17** (R_1 = Bu) are not miscible with perfluorohexane, whereas solubility of compounds **3**, **14** and **16** (R_1 = Me) in the same solvent increases with the length of the fluorous chain: it is estimated to be <0.1 M for **16** (C_4F_9 chain), ca. 0.3 M for **14** (C_6F_{13} chain) and >1 M for **3** (C_8F_{17} chain). These results demonstrate the need for a minimum F/H ratio to ensure compatibility of F-malonamides with common

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[†] The intermediate acids **11–13** can also be easily isolated as their potassium salts after concentration of crude saponification mixture in vacuo, followed by washing with ethanol and diethylether.

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