Heteroatom Chemistry
Volume 18, Number 5, 2007

Perfluoroketene Dithioacetals and Perfluorodithiocarboxylic Acid Derivatives: Versatile Tools for Organofluorine Synthesis

Charles Portella,[1] Murielle Muzard,[1] Jean-Philippe Bouillon,[1] Cédric Brulé,[1] Fabienne Grellepois,[1] Yuriy G. Shermolovich,[2] Vadim M. Timoshenko,[2] Alexander N. Chernega,[2] Enrique Sotoca-Usina,[3] Margarita Parra,[3] and Salvador Gil[3]

[1]*Unité Mixte de Recherche "Réactions Sélectives et Applications," CNRS—Université de Reims Champagne-Ardenne, UFR Sciences, BP 1039, 51687 REIMS Cedex 2, France*

[2]*Institute of Organic Chemistry, National Academy of Science of Ukraine, Murmanska str. 5, Kiev 02660, Ukraine*

[3]*Departamento de Química Orgánica, Facultat de Químicas, Universidad de Valencia, Dr. Moliner, 50, Burjassot 46100, Valencia, Spain*

Received 27 November 2006; revised 12 February 2007

ABSTRACT: *Perfluoroketene dithioacetals are simple and versatile compounds that can be transformed into a large variety of trifluoromethyl derivatives, in particular aza- and thiaheterocycles, perhalodithiocrotonic esters, and fluorinated dithiol thiones. These unsaturated perfluorodithioesters and analogs give interesting polar cycloaddition reactions whose mechanism is strongly influenced by the fluorine substitution. This substitution plays an important role in the reactivity of saturated perfluorodithiocarboxylic acids as well. Except for the carbophilic addition of allyl Grignard reagents to perfluorocarboxamides, a domino thiophilic addition-fluoride elimination was the main reaction process. Interestingly, a three-step domino reaction occurs when pentafluorodithioesters are treated with allyl Grignard reagents, the third step being an effective σ[3,3] rearrangement, so that the overall reaction is a formal substitution of an allyl group for the α-fluorine atom. 2,2-Bis(allyl)-3,3,3-trifluorodithiopropanoates were prepared by performing this domino reaction twice, in a possible one-pot procedure.* Heteroatom Chem 18:500–508, 2007; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20346

Correspondence to: Charles Portella; e-mail: charles.portella@univ-reims.fr

Present address of Jean-Philippe Bouillon: Laboratoire "Sciences et Méthodes Séparatives," EA 3233—Université de Rouen, IRCOF, F-76821 Mont Saint Aignan cedex, France.

Contract grant sponsor: Champagne-Ardenne Region.

Contract grant sponsor: French Ministry of Higher Education and Research.

Contract grant sponsor: European Commission.

Contract grant sponsor: National Academy of Science of Ukraine.

Contract grant sponsor: CEREP Company, Paris, France.

INTRODUCTION

Heteroelements play an important role in the field of organic chemistry. They can be used either to bring specific properties to a target molecule or as tools to perform reactions leading to the target molecule. While the chemistry and reactivity of each

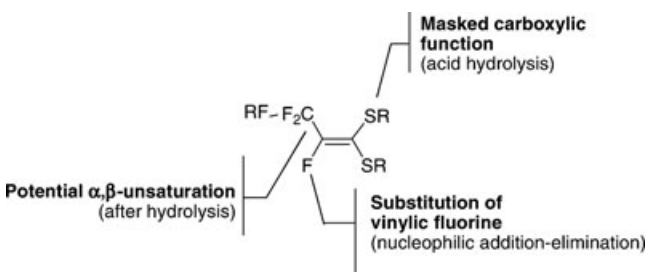
heteroelement is usually considered as a subdiscipline, combining the specific properties of different heteroelements can open a different field of investigation. This article presents a mixed organosulfur and organofluorine chemistry.

The specific properties of the fluorine atom explain the tremendous development of organofluorine compounds in various important fields such as polymers and materials, refrigerants, surfactants and liquid crystals, anesthetics, fluorous chemistry, agrochemicals, and pharmaceuticals [1]. Owing to its small size, its high electronegativity, and its ability to strongly bond with carbon, the introduction of fluorine atoms does not significantly affects the steric environment, but can highly modify the physicochemical and biological properties of the fluorinated molecules. The growing application of fluorinated bioactive compounds has favored the progress of organofluorine chemistry, but there is still a need for both increased knowledge in reaction mechanism and innovative methodologies for the synthesis of elaborated building blocks.

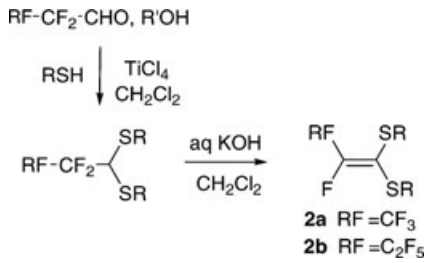
Several synthetically useful tools have been developed on the basis of organosulfur intermediates [2]. Indeed, sulfur can exist in various oxidation states, and its high polarizability induces unique features such as the stabilization of both positive and negative charges and polarity inversion (umpolung) reactivity [3].

THE CHEMISTRY OF PERFLUOROKETENE DITHIOACETALS

Perfluoroketene dithioacetals are highly versatile synthetic tools because they have both the interesting properties of their non-fluorinated analogs and others brought by the fluorine atoms. The potential reactivity of these building blocks is summarized in Scheme 1. Very few articles have been devoted to these types of compounds. Only the first member of the series have been reported [4], and we do not consider these difluoromethylene two-carbon compounds in this article. Only one attempt was made



SCHEME 1



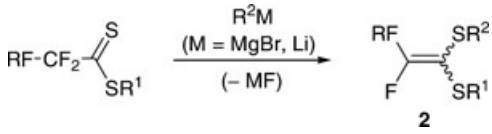
SCHEME 2

to prepare the higher three-carbon homolog, but no derived chemistry was reported, probably due to the low preparative value of the reaction (perfluoroalkene as the starting material and a poor (40%) yield) [5].

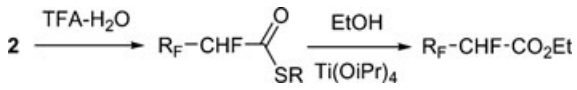
Preparation

The main route for synthons **2** consists of the thioacetalization of perfluoroaldehydes followed by HF elimination (Scheme 2). Both the hydrated and the hemiketal forms of the aldehyde may be used. Initially described for higher homologs ($RF = H(CF_2)_4$), using concentrated sulfuric acid and potassium hydroxide, respectively, for the two steps [6], we observed that titanium tetrachloride was the reagent of choice for performing the thioacetalization. Indeed, its reaction with the water or alcohol content releases hydrogen chloride, which itself is a good catalyst. The second step is performed under mild conditions using phase-transfer catalysts [7]. This methodology is well adapted for the first members of the series owing to the commercial availability of the perfluoroaldehydes, and remains a general and convenient method since the aldehydes can be prepared by lithium aluminum hydride reduction of perfluorocarboxylic esters [8].

In a different approach, perfluorodithiocarboxylic esters were converted into the corresponding ketene dithioacetals **2** by the thiophilic addition of an organometallic reagent, followed by the elimination of fluoride [9] (Scheme 3). Both lithium and magnesium reagents can be used. With an organomagnesium reagent, the distillation must be carried out after careful elimination of magnesium salts to avoid



SCHEME 3



SCHEME 4

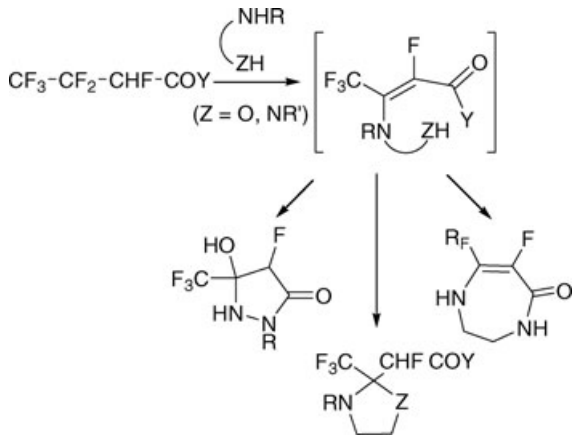
further reaction (*vide infra*). The chemoselectivity of this nucleophilic attack is obviously favored by the electron-withdrawing effect of fluorine and the subsequent β-fluoride elimination. The prior preparation of the perfluorodithioesters is needed in this approach [10].

Synthetic Applications

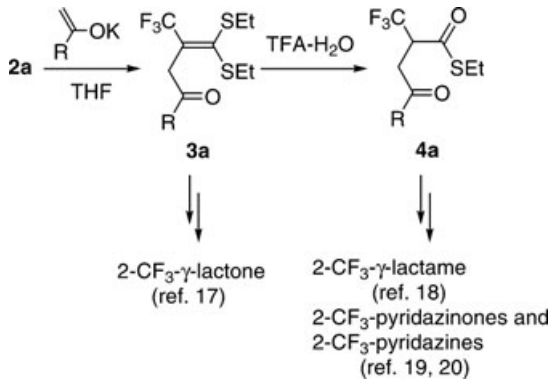
Perfluoroketene dithioacetals **2** behave as masked carboxylic acid derivatives. Indeed, acid hydrolysis leads to the corresponding 2-hydrothiol ester, which can be transesterified into an ester [7] (Scheme 4). α-Hydroperfluoroacid derivatives have previously been prepared by reactions of base with perfluoroalkenes [11].

2-Hydroperfluorobutanoates derived from **2b** are synthetic equivalents of both perfluorocrotonic acid derivatives and 2-hydro-3-oxo-perfluoroesters [12]. These compounds are valuable precursors for the corresponding enamino- or imino esters [13], as well as for polyfluorinated heterocycles such as pyrazole [14], oxazo- or imidazolidines, and diazepinones [15] (Scheme 5). The electron-withdrawing effect of the trifluoromethyl group favors an intramolecular Michael attack. It stabilizes the hydrated form of the pyrazolidinones as well.

The umpolung character of synthons **2** is an important feature that diversifies their reactivity. This is particularly interesting here due to the presence of a vinyl fluorine atom. Indeed, prior to any hydrolysis



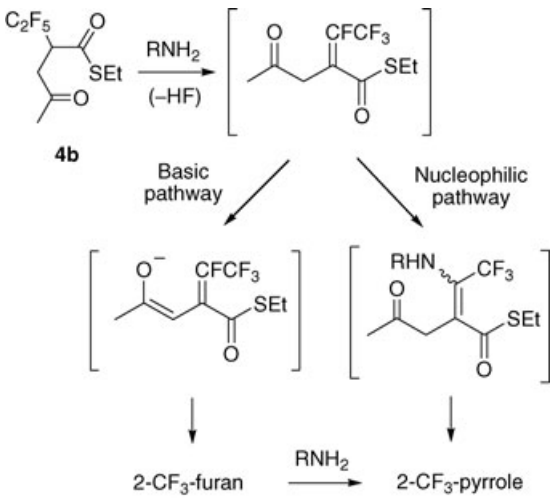
SCHEME 5



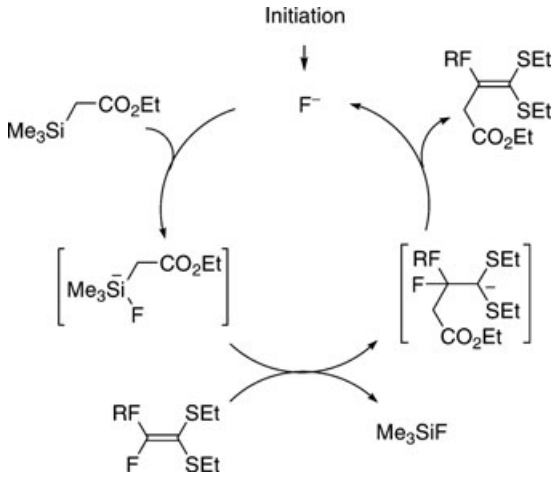
SCHEME 6

(normal reactivity, *vide supra*), it is easy to convert **2** into a masked α-perfluoroalkyl acid derivative by a nucleophilic addition-elimination process. This fluoride substitution may be carried out with simple heteroatoms or carbon-centered nucleophiles [16], but is much more interesting with functionalized ones such as ketone enolates. In this way, a variety of γ-keto derivatives **3** were prepared, thus opening the field of trifluoromethyl heterocycles (Scheme 6). Except γ-lactones [17], which result from a carbonyl reduction or an alkylation-hydrolysis sequence, hydrolysis of **3** to give the corresponding γ-keto-α-perfluoroalkyl thiol esters **4** is generally the first step toward nitrogen heterocycles [18–20] (Scheme 6).

Similarly, **2b** reacts with enolates to give **3b**, which is converted into **4b** by acid hydrolysis. When reacted with amines, this thiolester easily loses HF to give a new highly functionalized intermediate **5**, which, in turn, can react with amines via a basic or a nucleophilic pathway as depicted in Scheme 7.



SCHEME 7



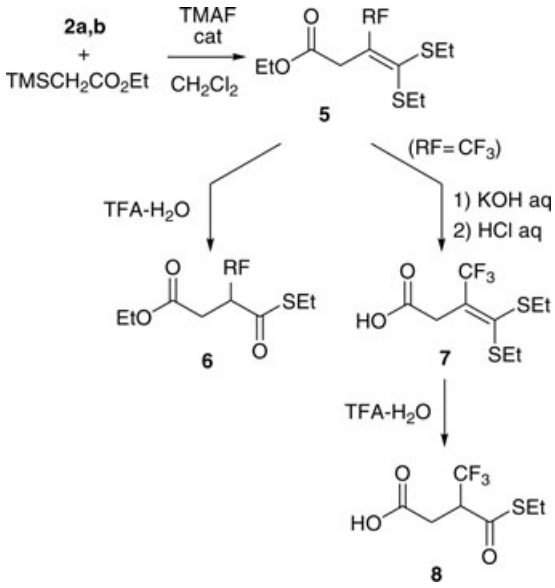
SCHEME 8

The subsequent cyclocondensation leads to a 2-trifluoromethyl pyrrole or 2-trifluoromethyl furan [21–23].

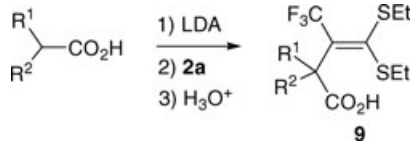
The reaction of **2** with an ester enolate is more problematic because the potassium or lithium enolate of ethyl acetate is either unreactive or decomposes to give a product where the vinylic fluorine is displaced by the ethoxide anion. Two different routes have been found to give access to α-perfluoroalkyl-1,4-dicarboxylic acid derivatives or synthetic equivalents. The first one consists of a chain reaction using ethyl(2-trimethylsilyl)acetate as a stabilized acetate enolate source. The reaction is initiated by a small quantity (5%) of tetramethyl ammonium fluoride. The driving chain-transfer step of this high yielding reaction results in the formation of the strong Si—F bond [24] (Scheme 8). The ketene dithioacetal moiety of the ester **5** is hydrolyzed under standard acidic conditions to give the diester **6**. The ester function of **5** may be selectively hydrolyzed, and the resulting acid **7** is transformed into the monoesterified succinic acid derivative **8** (Scheme 9).

While the lithium enolate function of ethyl acetate failed to react with **2**, a direct access to acid **7** and 3-substituted 2-trifluoromethyl succinic acid derivatives **9** was achieved using lithium enediolates as nucleophiles [24,25] (Scheme 10). Although simple work-up procedures using pH-controlled extractions were generally used [26], specific conditions had to be maintained to overcome the solubility problem inherent with these fluorinated species [25].

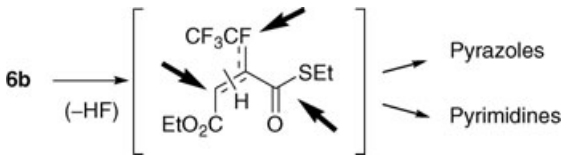
Compound **6b** (RF = C_2F_5) is easily dehydrofluorinated to give a Michael acceptor, which can react *in situ*. This intermediate possesses four electrophilic centers. It is noteworthy that only three of these centers are reactive toward substituted hydrazines



SCHEME 9

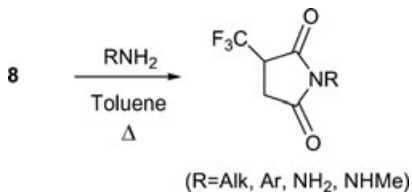


SCHEME 10

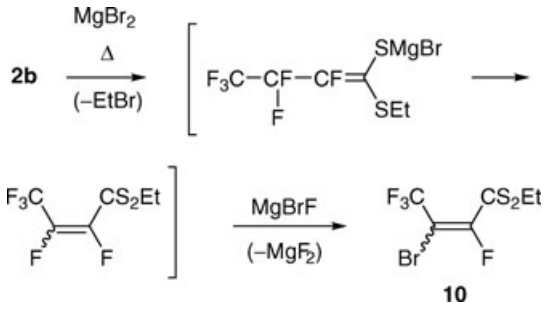


SCHEME 11

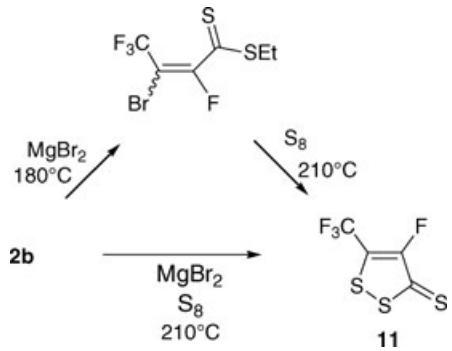
and amidines, allowing them to be converted into the corresponding 2-trifluoromethylated heterocycles (C. Brulé, J.-P. Bouillon, C. Portella, 2004 unpublished results) (Scheme 11). Compound **8** reacts with primary amines to give 2-trifluoromethyl succinimides [24] (Scheme 12).



SCHEME 12



SCHEME 13



SCHEME 14

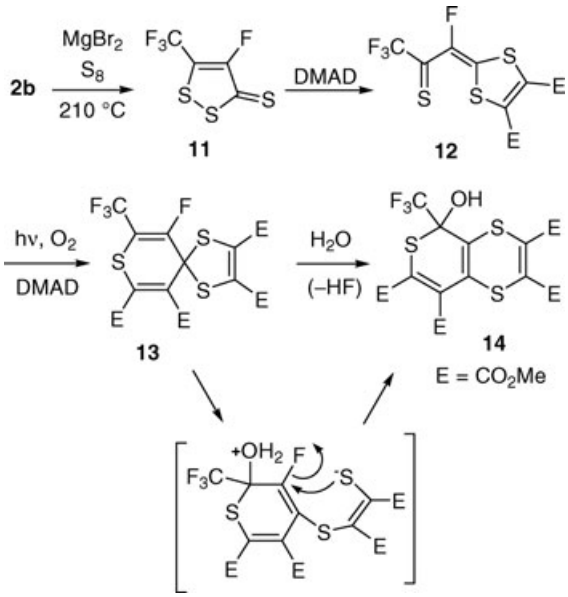
THE CHEMISTRY OF α,β-UNSATURATED PERFLUORODITHIOESTERS AND THEIR ANALOGS

Perhalodithiocrotonic Esters

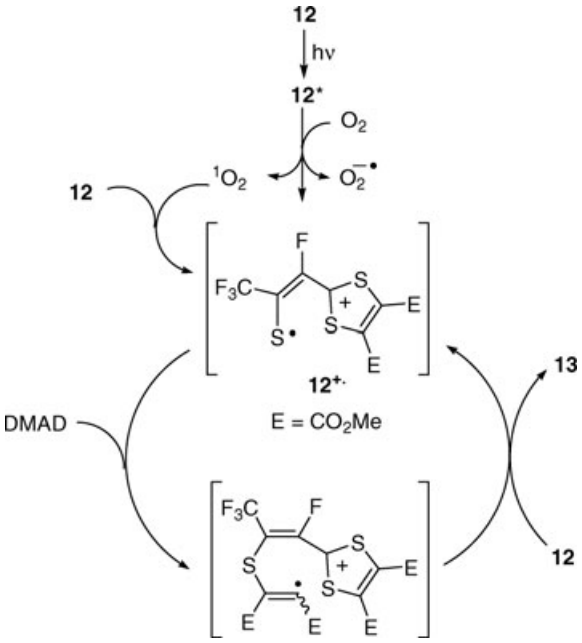
As previously mentioned, the thiophilic alkylation of perfluorodithiocarboxylic esters provided the opportunity for a subsequent transformation of **2b** while heating in the presence of magnesium salts [27]. This reaction was optimized to eventually provide the new perhalo unsaturated dithioester **10** [28] (Scheme 13). Compound **10** results from the nucleophilic attack of a bromide on the ethyl group, giving a magnesium perfluorodithioester enolate that easily loses the β-fluorine. A subsequent addition-elimination sequence results in the substitution of the vinyl fluorine by bromine [28]. This unsaturated dithioester has proven to be an interesting building block for the synthesis of trifluoromethyl thiaheterocycles.

5-Trifluoromethyl-1,2-dithiole-3-thione. A small quantity of 4-fluoro-5-trifluoromethyl-1,2-dithiol-3-thione **11** was produced under excessive heating, and it was assumed that molecular sulfur resulting from thermal decomposition could favor this reaction. This dithiolethione is indeed produced quantitatively when the dithiocrotonic ester is heated at 210°C with molecular sulfur. The conditions were optimized to achieve a high yielding synthesis of the 4-fluoro-5-trifluoromethyl-1,2-dithiole-3-thione **11** in a one-pot process from the corresponding perfluoroketene dithioacetal **2b** [29] (Scheme 14). Compound **11** behaves as an effective dienophile due to the presence of a C=S bond, as reported earlier for perfluorodithioesters [29].

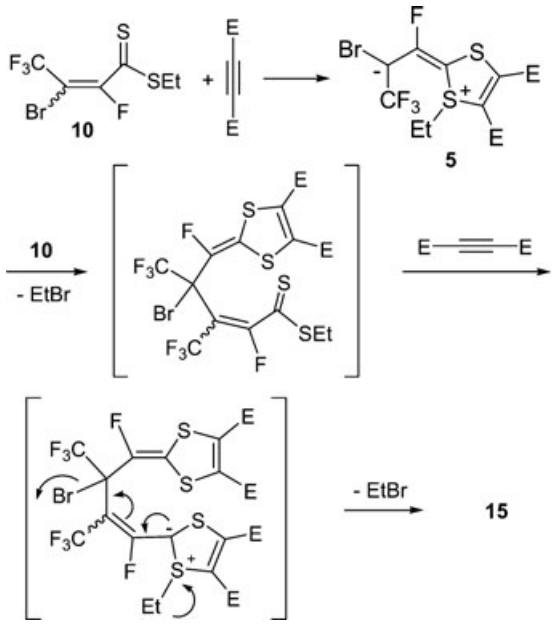
1,3-Dipolar Cycloaddition of Dithiocarboxylic Derivatives With Dimethylacetylene Dicarboxylate. As in the non-fluorinated series, 1,2-dithiol-3-thione **11** reacts with dimethylacetylene dicarboxylate (DMAD) in a 1,3-dipolar addition to give the 1:1 adduct **12**, which, in turn, reacts as an heterodiene with DMAD to give the 1:2 adduct **13** (Scheme 15). In contrast to the non-fluorinated series, where this transformation occurs via a thermal process, the second [4 + 2] cycloaddition occurred only in the presence of light and oxygen. A chain process initiated by a photoinduced single electron transfer to molecular oxygen was proposed to explain these observations [30] (Scheme 16). Such a mechanism seems relevant since the reaction can be induced by electrochemical oxidation in a dark and inert atmosphere (M. Medebielle, V. M. Timoshenko, J.-P. Bouillon, C. Portella, 2005 unpublished results). The 1:2 adduct reacts with water by simple filtration over silica gel, leading to the trithianaphtalene-type compound **14** via two successive addition-elimination sequences



SCHEME 15



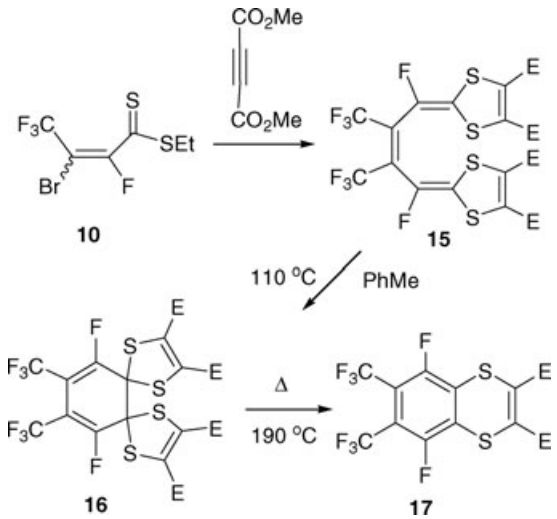
SCHEME 16



SCHEME 18

(Scheme 15). The detailed study of the reaction conditions gave access to an effective direct synthesis of either **12** or **13** from the dithiolethione **11**.

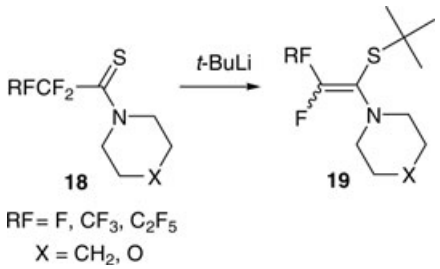
Similarly, the perhalodithiocrotonate **10** reacts with DMAD in a 1,3-dipolar cycloaddition, but the perhalo character of the substrate induces an unexpected pathway leading to the interesting vinyl analog of tetrathiafulvalene (TTF) **15** (Scheme 17). This compound results from a multi-step process involving the condensation of a primary adduct with the substrate **10** and a subsequent cycloaddition with DMAD [31] (Scheme 18). The TTF derivative **15** is quantitatively converted into the bis(spiro) compound **16**, which under stronger heating may be transformed into the benzodithiine **17** (Scheme 18). The latter may be directly prepared from the crotonic acid derivative **10**.



SCHEME 17

CHEMISTRY OF SATURATED PERFLUORODITHIOCARBOXYLIC ACID DERIVATIVES

The reactivity of dithiocarboxylic acid derivatives with nucleophiles is dominated by the duality of the thiophilic versus carbophilic attack on the thiocarbonyl group. Non-fluorinated thioamides react with organometallic reagents exclusively at carbon [32], except for the possible deprotonation of enolizable substrates [32d,33]. In the non-fluorinated series, the reaction of dithioesters with various nucleophiles has been extensively studied [2,34]. Because of the peculiar properties of the thiocarbonyl function, aliphatic Grignard reagents add selectively at sulfur [35], while allylic and vinylic Grignard reagents react exclusively at carbon [36]. In contrast, allylsilane adds to sulfur [37]. This apparent discrepancy in nucleophilic allylation can be explained by a metalloene-type mechanism in the case of allylmagnesium addition. We were interested in studying the reactivity of fluorinated analogs, and expected that the fluorine substitution would have a strong



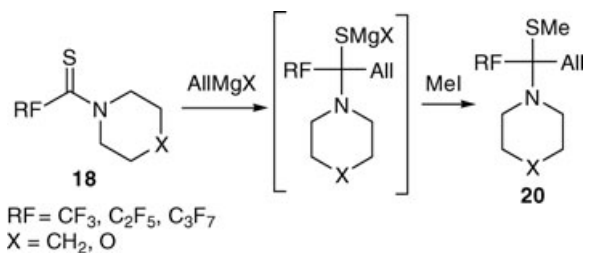
SCHEME 19

influence on the chemoselectivity of their reactions with nucleophiles. In addition, we anticipated that a thiophilic allylation combined with fluoride elimination would give a potential substrate for sigmatropic rearrangement.

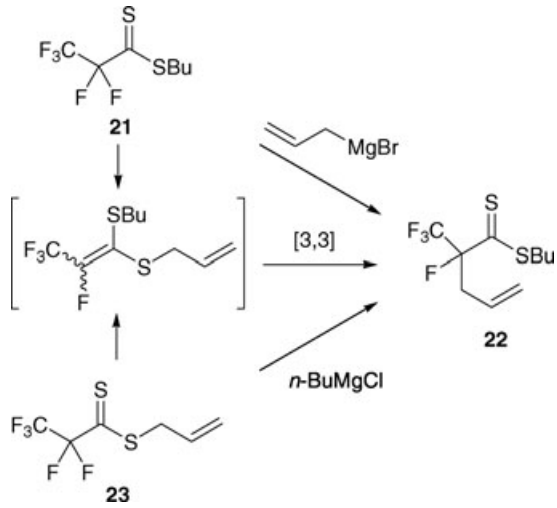
N,N-Dialkyl Perfluorocarboxylic Thioamides

The reaction of alkyllithium reagents with *N,N*-dialkyl perfluorocarboxylic thioamides **18** proceeds exclusively at sulfur, followed by the β-elimination of a fluoride to give the corresponding *N,S*-ketene acetals **19**, which are isolated in high yields [38] (Scheme 19).

Surprisingly, **18** proved to be inert when subjected to saturated organomagnesium reagents but reacted quantitatively with allyl Grignard reagents. As in the non-fluorinated series, due to both sulfur—magnesium coordination and a six-membered cyclic transition state, the reaction proceeds via a carbophilic attack. However, due to the presence of an electron-withdrawing perfluoroalkyl group, which stabilized the tetrahedral adduct, the corresponding *N,S*-acetals of type **20** were easily trapped with methyl iodide [38] (Scheme 20). The latter is converted into the corresponding dienamine via oxidation to sulfoxide, with subsequent elimination of sulfenic acid. In the absence of any trapping agent, the tetrahedral intermediate is formed via different pathways, which are under investigation.



SCHEME 20

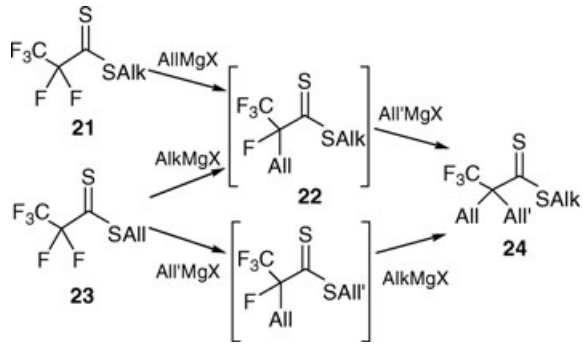


SCHEME 21

Pentafluorodithioesters: A New 3-Step Domino Reaction

As observed previously in the fluorinated series, allyl magnesium bromide reacts with sulfur to give the corresponding ketene dithioacetals **2** [9] (*vide supra*) owing to the presence of an electron-withdrawing group adjacent to the thiocarbonyl function. The same reactivity was observed for unsaturated phenyl and vinyl Grignard reagents [39]. Interestingly, while the allylic Grignard reagent reacted with the fluorinated dithioester **21** via a thiophilic addition, the expected ketene dithioacetal could not be isolated and underwent an *in situ* [3,3]-sigmatropic rearrangement [40] (Scheme 21). The absence of any intermediate ketene dithioacetal in the crude mixture is a significant proof of a non-reversible rearrangement, in comparison with what was observed in the non-fluorinated series [41]. As illustrated in Scheme 21, the mono(unsaturated) fluorinated dithioester **22** could also be reached by the reaction of alkyl magnesium halides with the *S*-allylic fluorinated dithioester **23** via the same three-step domino process: that is, thiophilic addition of the organomagnesium reagent, β-elimination of fluoride, followed by a [3,3]-sigmatropic rearrangement.

The last step of the domino reaction releases a dithioester moiety, thus a second domino reaction could also be performed. Despite the rapid formation of the intermediate *S*-allyl ketene dithioacetal, the rearrangement was found to be slower due to the bulky trifluoromethyl and allyl groups on the vinylic carbon and was accelerated by heating the reaction mixture [40]. Both symmetrical (All′=All) and unsymmetrical bis(unsaturated) compounds **24** were prepared via this approach. Furthermore, dithioesters



SCHEME 22

24 could be prepared in similar yields following a "one-pot" procedure starting directly from the pentafluorodithoesters such as **21** or **23** by the sequential addition of a suitable Grignard reagent [40] (Scheme 22).

CONCLUSION

The association of two very different heteroatoms, hard fluorine and soft sulfur, has led to a highly diversified mixed chemistry based on ketene dithioacetals and dithiocarboxylic intermediates. The presence of fluorine atoms confers interesting properties that lead to peculiar reactions and mechanisms, and eventually to the preparation of a wide variety of multifunctionalized organofluorine compounds.

ACKNOWLEDGMENTS

We thank University of Reims and the CNRS for their support. We are indebted to Dr Eric Nicolai for fruitful discussions, to the Bayer company for the generous gift of perfluoroalkyl(trimethyl)silane, to Jean-François Huot, Béatrice Hénin, Sylvie Lanthony, Henri Bailla, and Dominique Harakat for their assistance, and to Karen Plé for reviewing the manuscript.

REFERENCES

[1] (a) Kirsch, P. Modern Fluorine Chemistry: Synthesis, Reactivity, Applications; Wiley-Vch Verlag GmbH and Co. KGaA: Weinheim, 2004; (b) Hiyama, T. Organofluorine Compounds: Chemistry and Applications; Springer: New York, 2000; (c) Ojima, I.; McCarthy, J. R.; Welch, J. T. Biomedical Frontiers of Fluorine Chemistry; ACS Publications: Washington, DC, 1996; (d) Banks, R. E.; Smart, B. E.; Tatlow, J. C. Organofluorine Chemistry; Principles and Commercial Applications; Plenum Press: New York, 1994; (e) Filler, R.; Kobayashi, Y.; Yagupolskii, L. N. (Eds.). Organofluorine Compounds in Medicinal and Biochemical Applications; Elsevier: Amsterdam, 1993.

[2] (a) Page, P. (Ed.). Organosulfur Chemistry: Synthetic Aspects; Academic Press: London, 1995; (b) Metzner, P.; Thuillier, A. Sulfur Reagents in Organic Synthesis; Academic Press: London, 1994.

[3] (a) Kolb, M. Synthesis 1990, 171–190; (b) Gröbel, B.-T.; Seebach, D. Synthesis 1977, 357–402.

[4] (a) Tanaka, K.; Nakai, T.; Ishikawa, N. Chem Lett 1979, 175–178; (b) Gimbert, Y.; Moradpour, A. Tetrahedron Lett 1991, 32, 4897–4900; (c) Gimbert, Y.; Moradpour, A.; Dive, G.; Dehareng, D.; Lahlil, K. J Org Chem 1993, 58, 4685–4690; (d) Purrington, S. T.; Samaha, N. F. J Fluorine Chem 1989, 43, 229–234; (e) Purrington, S. T.; Sheu, K.-W. Tetrahedron Lett 1992, 33, 3289–3292; (f) Purrington, S. T.; Sheu, K.-W. J Fluorine Chem 1993, 65, 165–167; (g) Piettre, S.; De Cock, C.; Merenyi, R.; Viehe, H. G. Tetrahedron 1987, 43, 4309–4319.

[5] Sterlin, S. R.; Izmailov, V. M.; Isaev, V. L.; Shal, A. A.; Sterlin, R. N.; Dyatkin, B. L.; Knunyants, I. L. Zh Vses Khim Obshchest Im D I Mendeleeva 1973, 18, 710–712.

[6] Markovskii, L. N.; Slyusarenko, E. I.; Timoshenko, V. M.; Kaminskaya, E. I.; Kirilenko, A. G.; Shermolovich, Y. G. Zh Org Khim 1992, 28, 14–22; Chem Abstr 1992, 117, 150502.

[7] Muzard, M.; Portella, C. J Org Chem 1993, 58, 29–31.

[8] Pierce, O. R.; Kane, T. G. J Am Chem Soc 1954, 76, 300–301.

[9] Portella, C.; Shermolovich, Y. G. Tetrahedron Lett 1997, 38, 4063–4064.

[10] (a) Portella, C.; Shermolovich, Y. G.; Tschenn, O. Bull Soc Chim Fr 1997, 134, 697–702; (b) Babadzahanova, L. A.; Kirij, N. V.; Yagupolskii, Y. L. J Fluorine Chem 2004, 125, 1095–1098.

[11] For selected significant references, see (a) Nguyen, T.; Wakselman, C. J Fluorine Chem 1995, 74, 273–277; (b) Hu, C.; Tu, M. Chin Chem Lett 1992, 3, 87–90; Chem Abstr 1992, 117, 89814; (c) Ishihara, T.; Kuroboshi, M.; Yamaguchi, K. Chem Lett 1990, 211–214; (d) Nguyen, T.; Rubinstein, M.; Wakselman, C. J Fluorine Chem 1978, 11, 573–589; (e) Wakselman, C.; Nguyen, T. J Org Chem 1977, 42, 565–566; (f) Rendall, J. L.; Pearlson, W. H. US Patent 2862024 19581125, 1958; Chem Abstr 1959, 53, 50780; (g) Rendal, J. L.; Pearlson, W. H. US Patent 2795601 19570611, 1957; Chem Abstr 1957, 51, 90875; (h) Rendall, J. L.; Pearlson, W. H. UK Patent 737164 19550921, 1955; Chem Abstr 1956, 50, 74163.

[12] Iznaden, M.; Portella, C. J Fluorine Chem 1989, 43, 105–118.

[13] Portella, C.; Iznaden, M. J Fluorine Chem 1991, 51, 1–20.

[14] Portella, C.; Iznaden, M. Synthesis 1991, 1013–1014.

[15] Dondy, B.; Doussot, P.; Iznaden, M.; Muzard, M.; Portella, C. Tetrahedron Lett 1994, 35, 4357–4360.

[16] Muzard, M. Dithioacétals de cétènes fluorés: Synthèse et Réactivité. PhD dissertation, University of Reims: France, 1992.

[17] Huot, J.-F.; Muzard, M.; Portella, C. Syn Lett 1995, 247–248.

[18] Hénin, B.; Huot, J.-F.; Portella, C. J Fluorine Chem 2001, 107, 281–283.

[19] Brulé, C.; Bouillon, J.-P.; Nicolai, E.; Portella, C. Synthesis 2003, 436–442.

[20] Brulé, C.; Bouillon, J.-P.; Nicolaï, E.; Portella, C. Synthesis 2006, 103–106.
[21] Bouillon, J.-P.; Hénin, B.; Huot, J.-F.; Portella, C. Eur J Org Chem 2002, 1556–1561.
[22] Bouillon, J.-P.; Tinand, B.; Nuzillard, J.-M.; Portella, C. Synthesis 2004, 711–721.
[23] Bouillon, J.-P.; Kikelj, V.; Tinant, B.; Harakat, D.; Portella, C. Synthesis 2006, 1050–1056.
[24] Brulé, C.; Bouillon, J.-P.; Portella, C. Tetrahedron 2004, 60, 9849–9855.
[25] Sotoca, E.; Bouillon, J.-P.; Gil, S.; Parra, M.; Portella, C. Tetrahedron Lett 2004, 45, 8315–8317.
[26] (a) Brun, E. M.; Gil, S.; Mestres, R.; Parra, M. Synthesis 2000, 1160–1165; (b) Brun, E. M.; Gil, S.; Mestres, R.; Parra, M. Tetrahedron Lett 1998, 54, 15305–15320.
[27] Bouillon, J.-P.; Shermolovich, Y. G.; Portella, C. Tetrahedron Lett 2001, 42, 2133–2135.
[28] Timoshenko, V. M.; Bouillon, J.-P.; Shermolovich, Y. G.; Portella, C. Tetrahedron Lett 2002, 43, 5809–5812.
[29] Timoshenko, V. M.; Bouillon, J.-P.; Shermolovich, Y. G.; Portella, C. Tetrahedron Lett 2002, 43, 9963–9966.
[30] Timoshenko, V. M.; Bouillon, J.-P.; Chernega, A. N.; Shermolovich, Y. G.; Portella, C. Eur J Org Chem 2003, 2471–2474.
[31] Timoshenko, V. M.; Bouillon, J.-P.; Chernega, A. N.; Shermolovich, Y. G.; Portella, C. Chem Eur J 2003, 9, 4324–4329.
[32] (a) Beak, P.; Yamamoto, J.; Upton, C. J. J Org Chem 1975, 40, 3052–3062; (b) Tamaru, Y.; Harada, T.; Iwamoto, H.; Yoshida, Z. J Am Chem Soc 1978, 100, 5221–5223; (c) Tamaru, Y.; Harada, T.; Nishi, S.; Yoshida, Z. Tetrahedron Lett 1982, 23, 2383–2386; (d) Tominaga, Y.; Kohra, S.; Hosomi, A. Tetrahedron Lett 1987, 28, 1529–1532.
[33] Tamaru, Y.; Harada, T.; Nishi, S.; Mizutani, M.; Hioki, T.; Yoshida, Z. J Am Chem Soc 1980, 102, 7806–7808.
[34] For a review on thiocarbonyl compounds and dithioesters in particular, see Metzner, P. Synthesis 1992, 1185–1199.
[35] Léger, L.; Saquet, M. Bull Soc Chim Fr 1975, 657–666.
[36] Masson, S.; Saquet, M.; Thuillier, A. Tetrahedron 1977, 33, 2949–2954.
[37] Capperucci, A.; Degl'Innocenti, A.; Ferrara, M. C.; Bonini, B. F.; Mazzanti, G.; Zani, P.; Ricci, A. Tetrahedron Lett 1994, 35, 161–164.
[38] Timoshenko, V. M.; Shermolovich, Y. G.; Grellepois, F.; Portella, C. J Fluorine Chem 2006, 127, 471–475.
[39] Pfund, E.; Masson, S.; Vazeux, M.; Lequeux, T. J Org Chem 2004, 69, 4670–4676.
[40] Grellepois, F.; Timoshenko, V. M.; Shermolovich, Y. G.; Portella, C. Org Lett 2006, 8, 4323–4326.
[41] For an example of reversible thio-Claisen rearrangement of dithioester derivatives, see Metzner, P.; Pham, T. N.; Vialle, J. Tetrahedron 1986, 42, 2025–2036.