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Graphical Abstracts/J. Fluorine Chem. 128 (2007) 683–690

J. Fluorine Chem., 128 (2007) 699

A well feasible and general route to (organoethynyl)difluoroboranes, $R_HC{\equiv}CBF_2$, and their perfluorinated analogues, $R_FC{\equiv}CBF_2$

Vadim V. Bardin[a], Nicolay Yu. Adonin[a],
Hermann-Josef Frohn[b]

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[b]*Department of Chemistry, Inorganic Chemistry, University of Duisburg-Essen, Lotharstr. 1, D-47048 Duisburg, Germany*

$$K[RC{\equiv}CBF_3]_{(s)} + BF_{3(g)} \xrightarrow[-25\text{ to }-40\text{ °C}]{\text{PFP or PFB}} RC{\equiv}CBF_2\ (>90\%)$$

R = C_4H_9, $(CH_3)_3C$, CF_3, C_3F_7, $(CF_3)_2CF$, $CF_3CF{=}CF$, $C_4F_9CF{=}CF$, C_6F_5, PFP = $CF_3CH_2CHF_2$, PFB = $CF_3CH_2CF_2CH_3$

A well feasible and general route to (organoethynyl)difluoroboranes, $RHC{\equiv}CBF_2$, and their perfluorinated analogues, $RFC{\equiv}CBF_2$.

J. Fluorine Chem., 128 (2007) 703

Multi-step reactions of *N*-monosubstituted (polyfluoroalkane)thioamides with alkyllithium reagents

Sergiy S. Mikhailichenko[a], Alexander V. Rudnichenko[a],
Vadim M. Timoshenko[a], Alexander N. Chernega[a], Yuriy G. Shermolovich[a],
Fabienne Grellepois[b], Charles Portella[b]

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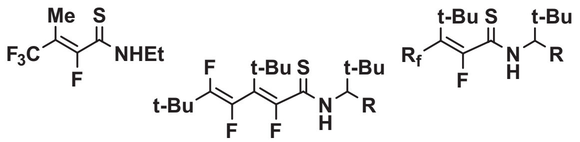


Reactions of *t*-BuLi or MeLi with *N*-alkylamides of polyfluoroalkanethioncarboxylic acids containing an α-proton on the *N*-alkyl substituent and a polyfluoroalkyl substituent larger than CF3 gave *N*-monosubstituted α,β-unsaturated fluorinated thioamides.

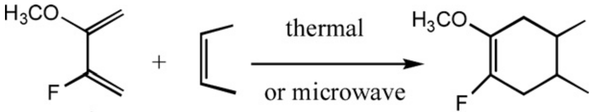
J. Fluorine Chem., 128 (2007) 710

Microwave assisted Diels-Alder cycloaddition of 2-fluoro-3-methoxy-1,3-butadiene

Timothy B. Patrick, Keith Gorrell, James Rogers

Department of Chemistry, Southern Illinois University, Edwardsville, IL 62026, USA

The title compound, **2**, undergoes Diels-Alder cyclization with a number of dienophiles. The reactions occur in moderate yield thermally, but occur in very good yield with microwave radiation.



2

3 - 10

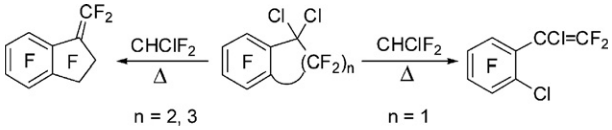
doi:10.1016/S0022-1139(07)00233-3

J. Fluorine Chem., 128 (2007) 714

The high-temperature alicyclic ring contraction of 1,1-dichloroperfluorotetralin and the alicyclic ring opening of 1,1-dichloroperfluorobenzocyclobutene

Victor M. Karpov, Tatyana V. Mezhenkova,
Vyacheslav E. Platonov

*N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry,
Novosibirsk 630090, Russia*



J. Fluorine Chem., 128 (2007) 718

Polyhalogenoheterocyclic compounds. Part 54: [1] Suzuki reactions of 2,4,6-tribromo-3,5-difluoropyridine

Hadjar Benmansour[a], Richard D. Chambers[a], Graham Sandford[a], Andrei S. Batsanov[b], Judith A.K. Howard[b]

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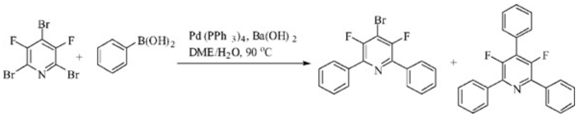

Palladium catalysed Suzuki cross-coupling reactions between 2,4,6-tribromo-3,5-difluoropyridine and aromatic boronic acid derivatives are reported

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J. Fluorine Chem., 128 (2007) 723

Trifluoromethylated cyclopropanes and epoxides from CuI-mediated transformations of α-trifluoromethyl-diazophosphonate

Igor D. Titanyuk[a], Irina P. Beletskaya[a], Alexander S. Peregudov[b],
Sergey N. Osipov[b]

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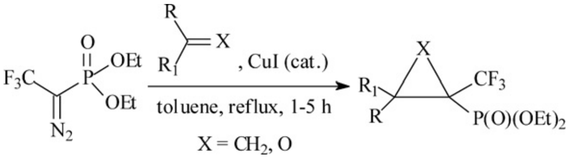
[b]*A.N. Nesmeyanov Institut of Organoelement Compounds, Russian Academy of Sciences, Vavilov str. 28, 119991 Moscow, Russia*



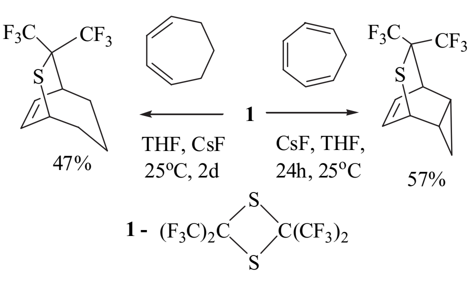
An efficient method for transformation of diethyl 1-diazo-2,2,2-trifluoroethylphosphonate to α-(trifluoromethyl)-cyclopropylphosphonates and α-(trifluoromethyl)-1,2-epoxyphosphonates has been developed.

J. Fluorine Chem., 128 (2007) 729

Hexafluorothioacetone based synthesis of fluorinated heterocycles

Viacheslav Petrov[a], Will Marshall[b]

[a]*DuPont Central Research and Development, P.O. Box 80328, Wilmington, DE 19880-0328, USA*[1]
[b]*DuPont Corporate Center for Analytical Sciences, Experimental Station, P.O. Box 80328, Wilmington, DE 19880-0328, USA*

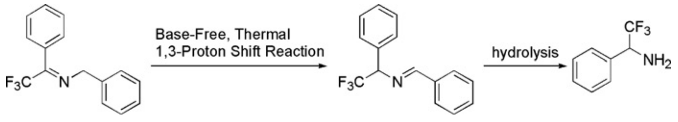


J. Fluorine Chem., 128 (2007) 736

Thermal 1,3-proton shift reaction and its application for operationally convenient and improved synthesis of α-(trifluoromethyl)benzylamine

Manabu Yasumoto, Hisanori Ueki, Vadim A. Soloshonok

Department of Chemistry and Biochemistry, University of Oklahoma,
Norman, OK 73019, United States



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Intramolecular cycloaddition of fluorinated 1,3,4-oxadiazoles to dienes

N.V. Vasil'ev[a,b], D.V. Romanov[b], A.A. Bazhenov[b], K.A. Lyssenko[c], G.V. Zatonsky[d]

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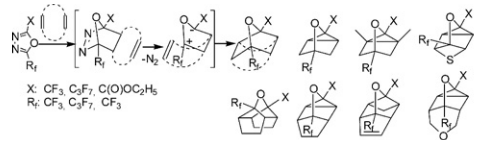
[c]*A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilova str. 28, 117813 Moscow, Russian Federation*
[d]*N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky prospect 47, 117913 Moscow, Russian Federation*



A number of acyclic and cyclic dienes, either conjugated or unconjugated, were studied in cycloaddition reactions with fluorinated 1,3,4-oxadiazoles. The reactions resulted in the products of both double cycloaddition (7-oxabicycloheptane compounds) and intramolecular cycloaddition (oxatricyclic and oxatetracyclic compounds). The structure of 4-(trifluoromethyl)-2-ethoxycarbonyl-1,6-dimethyl-3-oxatricyclo[2.2.1.0^{2,6}]heptane was confirmed by single crystal X-ray diffraction analysis.

J. Fluorine Chem., 128 (2007) 748

A new approach to fluorinated 4(3*H*)-quinazolinones

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Tatyana V. Trashakhova[a], Valerii N. Charushin[b]

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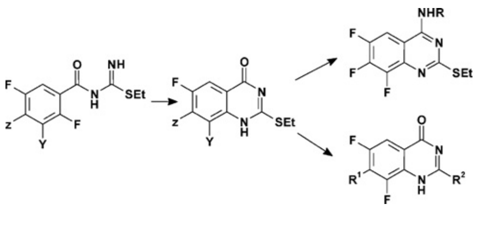
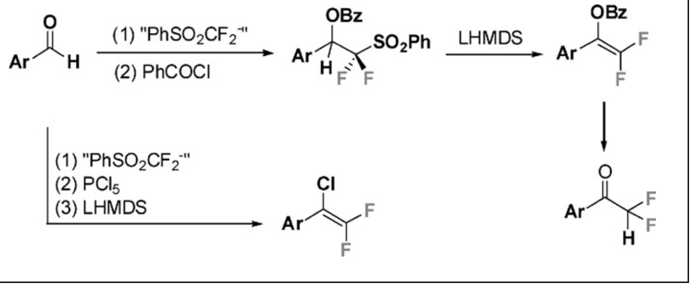


J. Fluorine Chem., 128 (2007) 755

Preparation of 1-aryl-2,2-difluoro enol esters via dehydrosulfonylation of α-(phenylsulfonyl)difluoromethylated benzoates

Laijun Zhang, Ya Li, Jinbo Hu

Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Feng-Lin Road, Shanghai 200032, China



J. Fluorine Chem., 128 (2007) 762

Fluorinated lithium 1,3-diketonates as reagents to modify podands and crown-ethers

Nadezhda S. Boltachova[a], Olga V. Fedorova[a], Irina G. Ovchinnikova[a], Olga N. Kazheva[b], Anatoliy N. Chekhlov[b], Oleg A. Dyachenko[b], Gennady L. Rusinov[a], Vera I. Filyakova[a], Valeriy N. Charushin[a]

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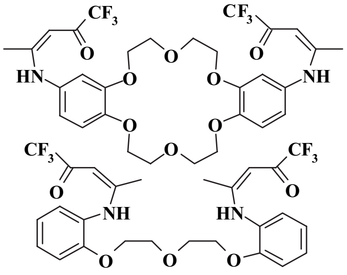

Fluorinated enaminoketones bearing two independent coordination centers (polyether's and fluorinated enaminoketones fragments) have been obtained. The crystal structure of Cu(II) complex of 1,5-bis-[2-(4′,4′,4′-trifluoro-1′-methyl-3′-oxo-but-1′-enylamino)phenoxy]-3-oxapentane (**10**) was studied by X-ray crystallography.

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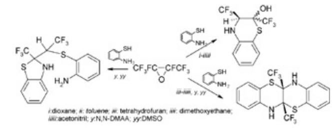
A route to fluorocontaining *N*,*S*-heterocycles *via* octafluoro-2,3-epoxybutane

Lyudmila V. Saloutina, Aleksandr Ya. Zapevalov, Victor I. Saloutin, Pavel A. Slepukhin, Mikhail I. Kodess, Valentina E. Kirichenko, Marina G. Pervova, Oleg N. Chupakhin

Institute of Organic Synthesis, Urals Branch of the Russian Academy of Sciences, 22/20 S. Kovalevskoy/Academicheskaya, GSP-147, 620041 Ekaterinburg, Russia



The reaction of octafluoro-2,3-epoxybutane with 2-aminothiophenol in dimethylsulfoxide and *N*,*N*-dimethylacetamide gave mainly 2-trifluoromethyl-2-[1-(2-aminophenylthio)-2,2,2-trifluoroethyl]-1,3-benzothiazolidine. A similar reaction in toluene, dioxane, tetrahydrofuran, dimethoxyethane and acetonitrile yielded 2,3-bis(trifluoromethyl)-3,4-dihydro-2*H*-1,4-benzothiazin-2-ol. Formation of minor 5a,11a-bis(trifluoromethyl)-5a,6,11a,12-tetrahydro-5,11-dithia-6,12-diazanaphthacene was observed in all solvents tested with the exception of toluene and dioxane. The molecular structure of the *RS*,*SR*-diastereomer of 2,3-bis(trifluoromethyl)-3,4-dihydro-2*H*-1,4-benzothiazin-2-ol, 5a,11a-bis(trifluoromethyl)-5a,6,11a,12-tetrahydro-5,11-dithia-6,12-diazanaphthacene and the *RS*,*SR*-diastereomer of 2-trifluoromethyl-2-[1-(2-aminophenylthio)-2,2,2-trifluoroethyl]-1,3-benzothiazolidine has been established by X-ray crystallography.

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The transformations of fluoroalkyl-containing 2-arylhydrazono-1,3-dicarbonyl compounds with methylamine

E.V. Shchegol'kov, Ya.V. Burgart, V.I. Saloutin

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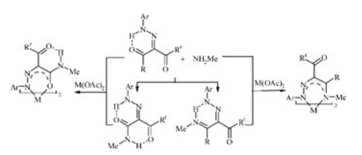

Fluoroalkylated 1,2,3-triketone 2-arylhydrazones and 2-arylhydrazono-3-oxo esters react variously with methylamine depending on the structure of the fluorinated substituent. 2-Arylhydrazono-1,3-dicarbonyl compounds having "short" fluoroalkyl substituents condense with methylamine at the carbonyl group attached to the non-fluorinated substituent whereas ones containing a lengthy polyfluoroalkyl substituent undergo haloformic cleavage as a result of the amine addition at the carbonyl group bearing such a substituent. The resulting 2-arylazo-3-(*N*-methyl)amino-1-polyfluoroket-2-en-1-ones and 1-(*N*-methyl)amino-2-arylhydrazono-3-fluoroalkyl-3-oxopropanamides have complexing properties, and they can bind to nickel(II) and copper(II) ions. Nickel chelates can be obtained by a three-component condensation of 2-arylhydrazono-1,3-dicarbonyl compounds and methylamine in the presence of nickel(II) cations.

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Amphiphilic perfluoroalkylated sulfones and sulfonate betaines

Robert Kaplánek, Oldřich Paleta

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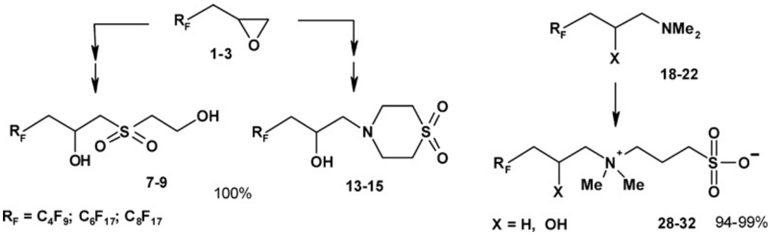


Convenient synthesis of 3-fluoro-4,5-diphenylfuran-2(5*H*)-one from

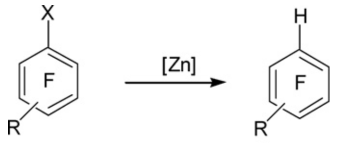
J. Fluorine Chem., 128 (2007) 797

Recent advances in practice and theory of polyfluoroarene hydrodehalogenation

Vitalij D. Shteingarts

N.N. Vorozhtsov Institute of Organic Chemistry, Siberian Division of Russian Academy of Sciences, 630090 Novosibirsk, Russia

Concise and highly selective ways from readily available polyfluoro to much less accessible partially fluorinated arenes via hydrodehalogenation by means of reductive systems based on zinc are reviewed.



X = F, Cl

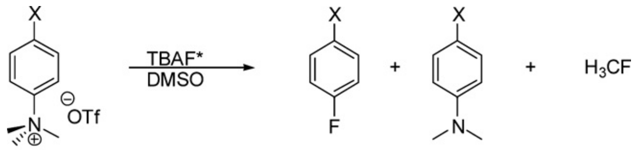
J. Fluorine Chem., 128 (2007) 806

Competitive demethylation and substitution in *N*,*N*,*N*-trimethylanilinium fluorides

Haoran Sun, Stephen G. DiMagno

Department of Chemistry and Nebraska Center for Materials and Nanoscience, University of Nebraska, Lincoln, NE 68588-0304, USA

Fluorinations of trimethylanilinium triflates are complicated by competing, and exceptionally facile S_N2 reactions in DMSO under anhydrous conditions.



X = NO_2, CHO, CN, COPh, CF_3, CO_2CH_3, Br, H, CH_3, OCH_3

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Fluoride-mediated selective cross-coupling reactions of alkyl halides and trimethyl(perfluoroalkyl)silanes, Me_3SiR_f ($R_f = CF_3$, C_2F_5) in the absence of any catalysts

Wieland Tyrra[a], Dieter Naumann[a], Silke Quadt[a], Sigrid Buslei[a], Yurii L. Yagupolskii[b], Mikhail M. Kremlev[b]

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[b]*Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Murmanskaya St. 5, UA-02094 Kiev, Ukraine*

$$\underset{\mathbf{1}}{C_nH_{2n+1}X} + Me_3SiCF_3 + [Cat]F \xrightarrow[-18^{\circ}C\ \text{to r.t.}]{DME} \underset{\mathbf{2}}{C_nH_{2n+1}CF_3} + Me_3SiF + [Cat]X,$$

X = Br, I; Cat = NMe_4, $S(NMe_2)_3$, $Cs(15\text{-Crown-}5)_2$;

$$\underset{\mathbf{1}}{C_nH_{2n+1}I} + Me_3SiC_2F_5 + [Cs(15\text{-Crown-}5)_2]F \xrightarrow[-18^{\circ}C\ \text{to r.t.}]{DME} \underset{\mathbf{3}}{C_nH_{2n+1}C_2F_5} + Me_3SiF + [Cs(15\text{-Crown-}5)_2]I.$$

J. Fluorine Chem., 128 (2007) 818

Synthesis and Diels–Alder reactions of α-fluoro- and α-trifluoromethylacrylonitriles

Valentine G. Nenajdenko[a], Vasiliy M. Muzalevskiy[a], Aleksey V. Shastin[b], Elizabeth S. Balenkova[a], Günter Haufe[c]

[a]*Moscow State University, Department of Chemistry, Leninskie Gory, Moscow 119992, Russia*
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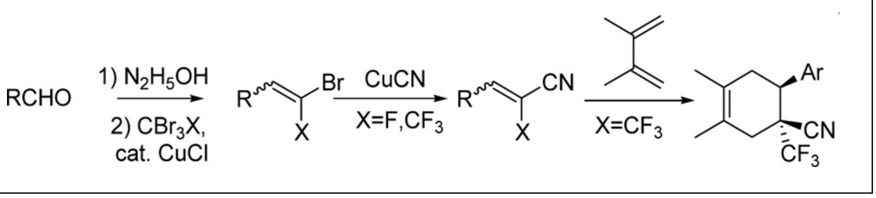
[c]*Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster, D-48149 Münster, Germany*

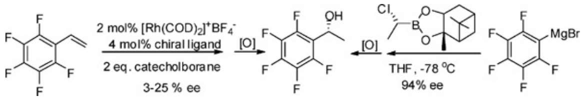


J. Fluorine Chem., 128 (2007) 827

Asymmetric hydroboration and Matteson homologation for the preparation of fluorinated α-phenethanols

P. Veeraraghavan Ramachandran, Michael P. Jennings

Herbert C. Brown Center for Borane Research, Department of Chemistry, Purdue University, 560 Oval Drive, West Lafayette, IN 47907-2084, United States



The catalytic hydroboration–oxidation of ring-fluorinated styrenes (F-PhCH=CH_2) was achieved with catecholborane along with a combination of $[Rh(COD)_2]^+BF_4^-$ and (*R*)-BINAP providing 81–96% enantioselectivities for the product alcohols for *ortho*-unhindered styrenes. A deleterious effect of a 2,6-disubstitution on the enantioselectivity of the product alcohol was observed. 2-Trifluoromethylstyrene also provides only 53% ee, probably due to the steric bulk of the CF_3 group at the *ortho*-position of styrene. Asymmetric homologation of fluorophenylmetals (magnesium bromide or lithium) with pinanediol α-chloroethylboronate, followed by oxidation readily furnished the desired 1-(2,6-difluorophenyl)- and 1-(perfluorophenyl)ethanols in 94–95% ee.

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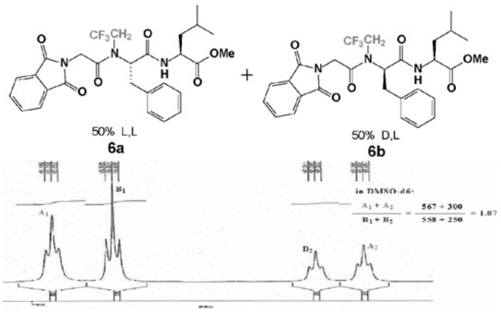
The first example of linear peptides containing a *N*-trifluoroethylated backbone amide linkage and the surprising solution dynamics observed by ^{19}F NMR

Changqing Lu, Darryl D. DesMarteau

Department of Chemistry, Clemson University, Clemson, SC 29634, USA



^{19}F NMR (21 °C, DMSO-d_6) of the two diasteromers of tripeptide **6**.

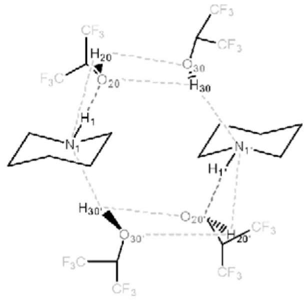
J. Fluorine Chem., 128 (2007) 839

A crystalline H-bond cluster of hexafluoroisopropanol (HFIP) and piperidine. Structure determination by X ray diffraction

J.-F. Berrien[a], M. Ourévitch[a], G. Morgant[a], N.E. Ghermani[b], B. Crousse[a], D. Bonnet-Delpon[a]

[a]*BioCIS, UMR CNRS 8076, IFR 141, Faculté de Pharmacie Univ. Paris-Sud, 5 rue J.B. Clément, 92296 Châtenay-Malabry, France*

[b]*Laboratoire PPB, UMR CNRS 8612, IFR 141, Faculté de Pharmacie Univ. Paris-Sud, 5 rue J.B. Clément, 92296 Châtenay-Malabry, France*



Piperidine and 1,1,1-3,3,3 hexafluoro-2-propanol (HFIP) have been co-crystallized. Single-crystal X-ray analysis displays the existence of hydrogen bonding aggregates through dimers **1** of the complex [one piperidine/two HFIP) where the heteroatoms form a six-center ring. Each heteroatom is multiple H-bond donor and acceptor and the system forms supramolecular architecture.

J. Fluorine Chem., 128 (2007) 844

The influence of fluorine on the asymmetric reduction of fluoromethyl ketones

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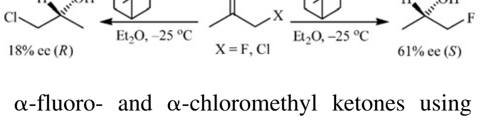
Herbert C. Brown Center for Borane Research, Department of Chemistry, Purdue University, 560 Oval Drive, West Lafayette, IN 47907-2084, United States



A comparative study of the asymmetric reduction of representative aryl and alkyl α-fluoro- and α-chloromethyl ketones using (−)-diisopinocampheylchloroborane [(−)-DIP-Chloride™] and (−)-*B*-isopinocampheyl-9-borabicyclo[3.3.1]nonane [*R*-Alpine-Borane®] has been made. It was observed that DIP-Chloride™ is superior in terms of the rate and enantioselectivity for both classes of halo-ketones. While the reduction of monofluoroacetone and trifluoroacetone with DIP-Chloride™ provided the product alcohols in 61% ee and 96% ee, respectively, the reduction of difluoroacetone yielded only 5% ee. The influence of a lone halogen atom was not observed for monochloroacetone, all of which point towards a chelating effect in the presence of the Lewis acidic chloroborane.

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A new preparation of trifluoromethanesulfinate salts

Bernard R. Langlois[a,b,c,d,e], Thierry Billard[a,b,c,d,e],
Jean-Christophe Mulatier[a,b,c,d,e], Catherine Yezeguelian[a,b,c,d,e]

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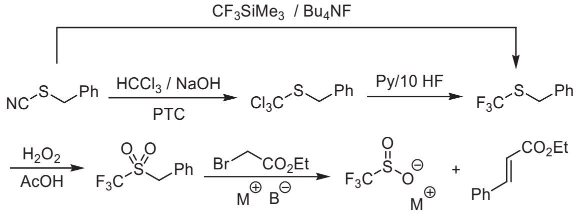
[b]*CNRS, UMR5246, Villeurbanne F-69622, France*
[c]*Université de Lyon 1, Lyon F-69622, France*
[d]*INSA-Lyon, Villeurbanne F-69622, France*
[e]*CPE Lyon, Villeurbanne F-69616, France*



Various trifluoromethanesulfinates can be easily prepared from benzyl thiocyanate.

J. Fluorine Chem., 128 (2007) 857

A qualitative scale for the electron withdrawing effect of substituted phenyl groups and heterocycles

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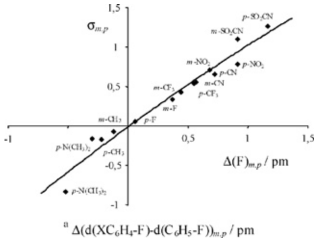

On the basis of DFT calculations, the electron withdrawing effect of a variety of F, O^- or NH^- substituted phenyl groups and heterocycles can be classified by the corresponding C–E bond lengths (E = F, O^- or NH^-).
The defined constants $\Delta(E)_{m,p}$ – the difference of the E–C bond lengths of the substituted derivatives X-C_6H_4-E and the non-substituted phenyl derivative, C_6H_5-E – exhibit the same tendency as the corresponding Hammett constants ($\sigma_{m,p}$). The values of $\Delta(E)_{m,p}$ strongly depends on the nature of E. With E = F, the resulting values $\Delta(F)_{m,p}$ are found to be accidentally close to the corresponding Hammett constants.

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Synthesis of new pentafluorosulfanylacrylates ($F_5SCH{=}CHCHO$, $F_5SCH{=}CHCN$, $F_5SCH{=}CHCOOCH_3$) and use of them as dienophiles in Diels-Alder reaction

Valery K. Brel

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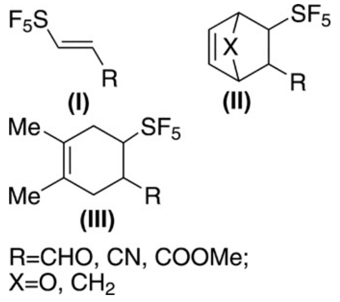

New pentafluoro-λ^6-sulfanylacrylates (**I**) were synthesized by a convenient and efficient method. These compounds are useful as intermediates in the preparation of pentafluoro-λ^6-sulfanyl-containing cyclic, and heterocyclic Diels-Alder cycloadducts (**II**) and (**III**).

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Trifluoromethyl-containing *N*-acylmethylenequinone imines as novel highly electrophilic agents

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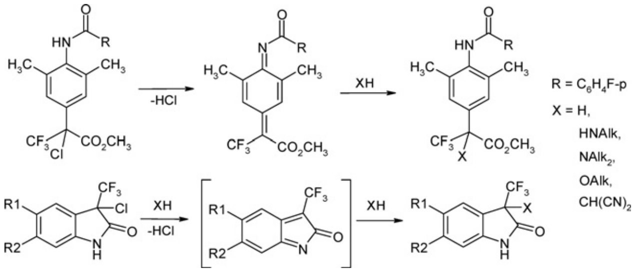

The first highly electrophilic CF_3-containing agents of the *N*-acylmethylenequinone imine class have been prepared. Their reactions with N-, O-, and C-nucleohiles have been studied.

J. Fluorine Chem., 128 (2007) 879

A facile synthesis and herbicidal activities of novel fluorine-containing thiazolo[4,5-*d*]pyrimidin-7(6H)-ones

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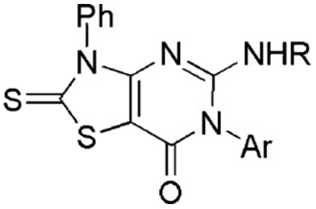

Novel thiazolo[4,5-*d*]pyrimidine derivatives were designed and synthesized *via* a facile regioselective cyclization process. Bioassay indicated that most of the compounds showed significant herbicidal activities.