Organic halides

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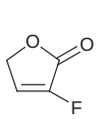
Previous review: *J. Chem. Soc., Perkin Trans. 1*, 1998, 1577

1 Introduction

This article continues the series of reviews on the synthesis of organic halides previously published in Contemporary Organic Synthesis and Perkin Transactions 1.[1] The aim is to present important new and topical methods for the preparation of organic halides, in particular those which have advantages over existing methods, either in terms of yield, selectivity or practicality. The same format from previous reviews has been retained, and will follow the different types of organic halide laid out above. The importance of organofluorine compounds has again been evident this year. A review on the chemistry of glycosyl fluorides has been published.[2] Several new reagents and intermediates have also been reported this year. Caesium fluoroxysulfate has been used to convert primary alcohols to acyl fluorides,[3] and 2-fluorobut-2-en-4-olide **1** has been presented as a new fluorinated synthon. 4,4-Dibromo-3-methylpyrazol-5-one **2** has been utilised in the selective monobromination of phenols,[4] and 1-(*p*-tolylsulfonyloxy)-1,2-benziodoxol-3(1*H*)-one **3** has been used in the selective iodination of benzene rings.[5]



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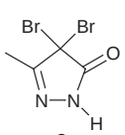

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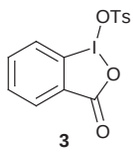

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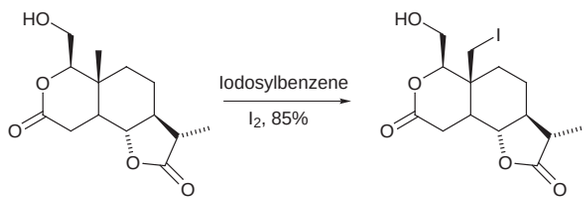
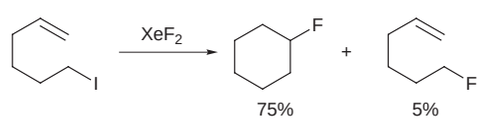
2 Alkyl halides

2.1 By halogenation of alkanes and alkenes

Relatively few reactions on the halogenation of alkenes have been reported this year, so these two sections have been combined. Liguori *et al*. have reported a direct homolytic iodination reaction of alkanes by perfluoroalkyl iodides.[6] During the synthesis of (+)-8-deoxyvenolepin, Astudillo *et al*. used iodosylbenzene to functionalise a methyl group (Scheme 1).[7] A novel,

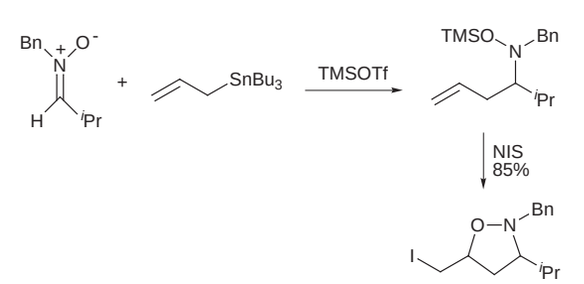


Scheme 1

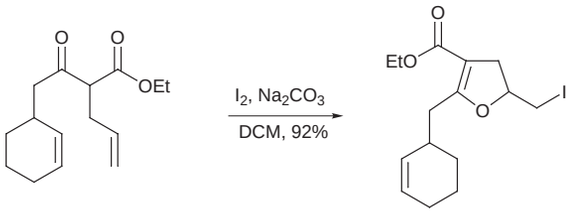


Scheme 2

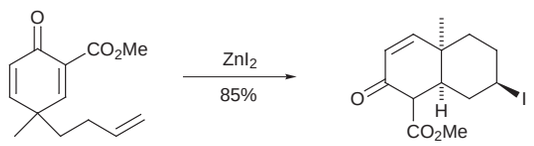
direct route to 2-deoxy-2-fluoroaldoses and derivatives has been described using the SelectFluor™ reagent.[8] Patrick and Zhang have used xenon difluoride to promote a deiodinative fluorination reaction (Scheme 2).[9] The reaction proceeded with loss of iodine, cyclisation and incorporation of fluorine. Novel types of liquid crystal based on axially fluorinated cyclohexane units have been reported.[10] Tyrell and co-workers have used Nicholas carbocation methodology in a diastereoselective synthesis of benzopyrans.[11] Kobayashi and Miki have published a synthesis of norbornadiene fused heterocycles which includes bromination reactions to give methanopuinoxaline derivatives.[12] Paquette has used a bromination–destannylation procedure during the total synthesis of spinosyn A.[13] Bailey and Carson have shown that phenyllithium can be used in catalytic amounts to facilitate the cycloisomerisation of 6-iodohex-1-enes to cyclopentanes.[14] Gionotti *et al*. have reported a one pot synthesis of 5-iodomethylisoxazolidines (Scheme 3).[15] Trimethylsilyl trifluoromethanesulfonate promoted addition of allyl stannane to aldonitrones was followed by cyclisation onto the alkene. The formation of dihydrofurans from 1,3-dicarbonyl compounds has been reported.[16] The iodine promoted cyclofunctionalisation gave the desired compounds in good yields and under mild conditions (Scheme 4). Liu and Sun have described the total synthesis of (±)-dehydrochamaecynenol.[17] The key step was the polyene cyclisation promoted by the cross conjugated α-alkoxycarbonyl enone system (Scheme 5). The synthesis of pyrrolidones has been achieved by a triethylborane mediated atom transfer cyclisation (Scheme 6).[16] During the synthesis of (+)-epoxydictymene, Paquette and co-workers employed a stereoselective hydrobromination reaction (Scheme 7).[19]



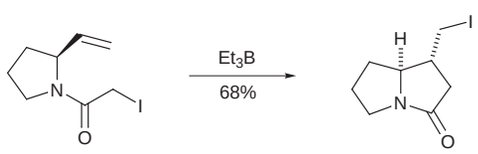
Scheme 3



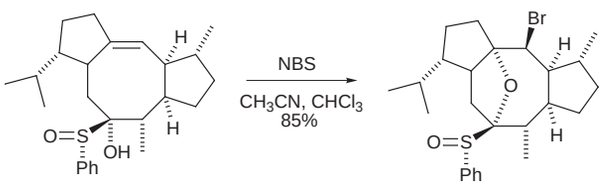
Scheme 4



Scheme 5



Scheme 6



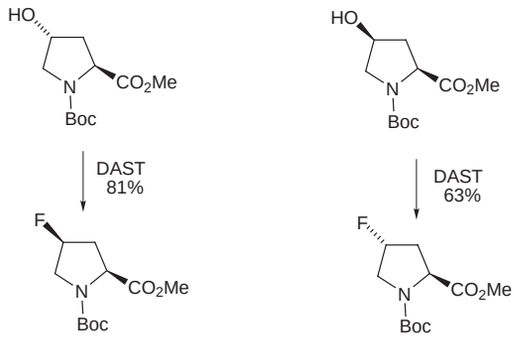
Scheme 7

2.2 By nucleophilic substitution

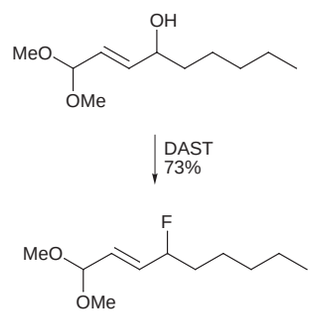
The use of DAST to transform hydroxy groups to fluorides remains a popular procedure. Two examples are the synthesis of protected proline derivatives from the corresponding alcohols[20] (Scheme 8) and the production of fluorinated analogues of polyunsaturated fatty acids (Scheme 9).[21] A new preparative route to organic halides from alcohols *via* the reduction of polyhalomethanes has been reported.[22] Ceccherelli *et al*. have converted oximes to *gem*-chloro-nitro derivatives in a one step process (Scheme 10).[23] The preparation of chloromethylphenyl solid supports has been achieved by taking the commercially available alcohol and reacting with methanesulfonyl chloride and Hunig's base to give a quantitative yield of the required polymer bound intermediate.[24] A facile synthesis of chloromethyl substituted cinnamyl derivatives has been reported (Scheme 11).[25] The reaction did not produce the expected mesylated product, and presumably proceeds *via* an S_N2' pathway. The conversion of thiols and disulfides to chlorides has also been described.[26] The direct conversion of silyl ethers to the corresponding bromides has been shown to occur with inversion of configuration.[27] Perciás and co-workers selectively transformed the alcohol **4** to the iodide during the enantioselective construction of angularly fused triquinanes (Scheme 12).[28] The use of α-halo enolates as nucleophiles has provided routes to substituted amides and lactones. Myers and co-workers have outlined a practical methodology for the asymmetric synthesis of organofluorine compounds from the corresponding amide (Scheme 13).[29] A stereoselective synthesis of α-fluoroamides using a germyl anion species has been reported,[30] and α-chloro-β-lactones have been prepared by an aldol reaction with lithium ester enolates derived from chlorinated phenyl alkanoates (Scheme 14).[31]

2.3 By electrophilic substitution

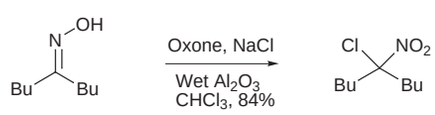
Enders and co-workers have devised a regio- and enantio-



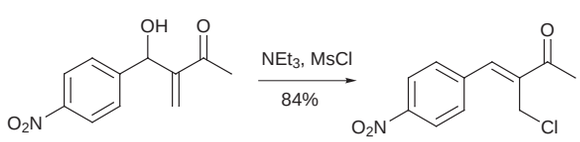
Scheme 8



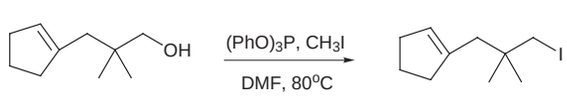
Scheme 9



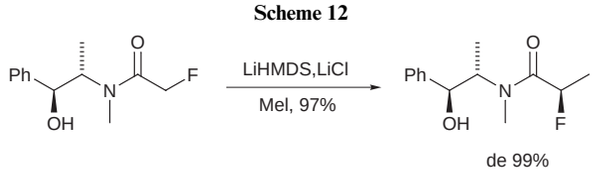
Scheme 10



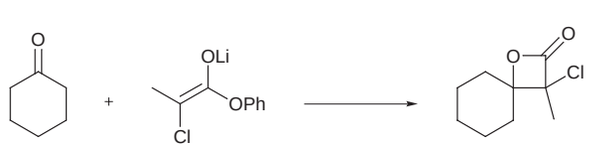
Scheme 11



Scheme 12

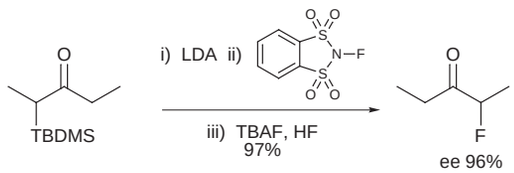


Scheme 13

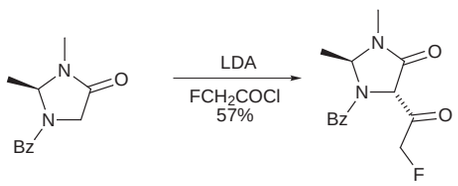


Scheme 14

selective synthesis of α-fluoro ketones by electrophilic fluorination of α-silylketone enolates with *N*-fluorobenzosulfonamide (Scheme 15).[32] A new versatile chiral derivatising reagent, α-cyano-α-fluoro-*p*-tolylacetic acid (CFTA) has been reported.[33] Amin *et al*. have synthesised the fluorinated natural product (2*S*,3*S*)-4-fluorothreonine.[34] The highly stereoselective synthesis incorporates the fluoride using an acid chloride as an electrophilic quench (Scheme 16). Hoffman and Tao have

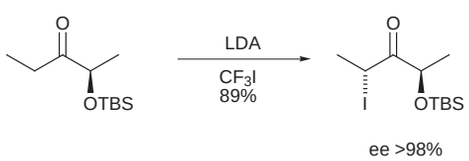


Scheme 15



Scheme 16

synthesised monofluorinated amides for use as dipeptide isosteres.[35] A synthesis of 2′-fluoro substituted carbovir has been reported,[36] as has a highly selective synthesis of α-monofluoro and chlorobenzylphosphonates.[37] Enders has also reported an asymmetric synthesis of α-iodo ketones using iodotrifluoromethane as the electrophilic quench (Scheme 17).[38]



Scheme 17

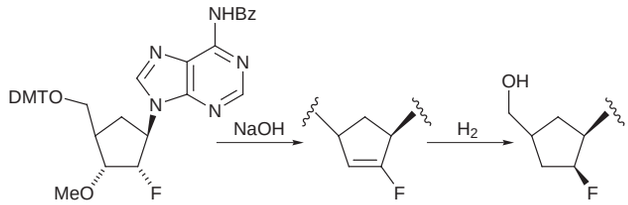
2.4 By other methods

Marquez has described a new synthetic approach to clinically useful anti-HIV active nucleosides (Scheme 18).[39] The 2′β-fluoro substituent was introduced *via* inversion of the readily available 2′α-fluoro isomer. Bravo and co-workers have reported the stereoselective synthesis of the antibacterial 3-fluoro-D-alanine.[40] An enantiomeric synthesis of 3-fluoro-apionucleosides has been reported.[41] The [3,3] sigmatropic rearrangement proceeds in good yield and with enantiomeric excess (Scheme 19). Funabiki *et al*. have provided the first efficient and convenient access to α-fluoro-β,β-dialkoxy ketones.[42] Two routes to α-fluoro ketones from β-keto esters have been reported.[43,44] Both incorporate the fluoride into the activated methylene position of the β-keto ester, and perform a decarboxylation to produce the desired products. Nickel powder has been used to mediate radical cyclisation routes to β- and γ-lactones[45] including a concise construction of the mesembrine skeleton (Scheme 20). Similar chemistry has also been reported using tributyltin hydride and triethylborane, although alternative products were found depending on the reaction conditions (Scheme 21).[46] Chloro substituted cyclopropanes have been accessed by an electroreductive coupling of activated olefins with *gem*-polyhalide compounds.[47] Garg and Lee have found a regioselective method for the bromomethylation of 1,2-dialkybenzenes (Scheme 22).[48] Precursors of novel amino acids have been prepared by the asymmetric synthesis of (2*S*)-ω-bromo-azido acids.[49] A samarium diiodide promoted diiodomethylation of carbonyl compounds has been reported.[50] When treated with base, the products can be transformed into α-iodo aldehydes (Scheme 23). Treatment of 1,1-diallyl-2-amino alcohols with iodine has led to a synthesis of optically active pyrrolidines (Scheme 24).[51]

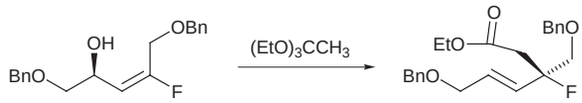
3 Vinyl halides

3.1 From alkynes

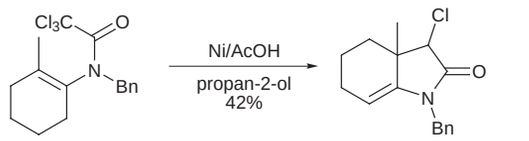
A few notable preparations of vinylic iodides from alkynes have



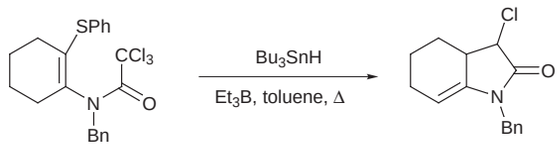
Scheme 18



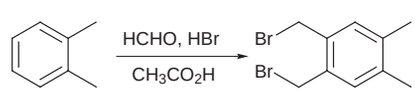
Scheme 19



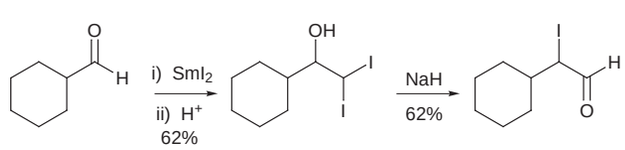
Scheme 20



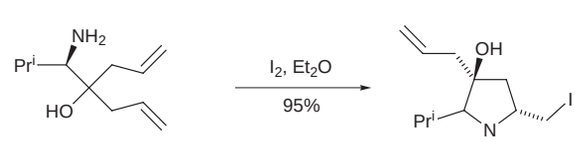
Scheme 21



Scheme 22

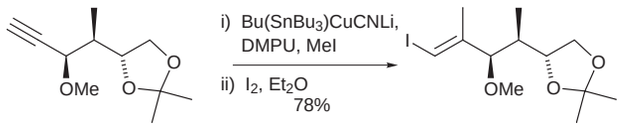


Scheme 23

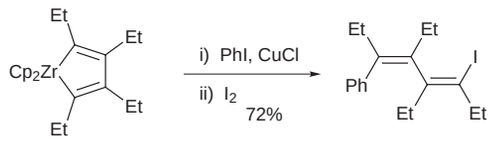


Scheme 24

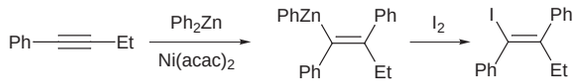
appeared this year. White and co-workers employed a stannyl cuprate addition to a triple bond, followed by iodine quench on the way to a total synthesis of the macrolide antitumour agent rhizoxin (Scheme 25).[52] The use of transition metals to perform coupling reactions across alkynes continues to be of prime importance. Takahashi has used a zirconium mediated alkyne coupling protocol and then performed two more reactions on the intermediate (Scheme 26).[53] The initial zirconacycle, made from the corresponding alkyne, was reacted with iodobenzene then quenched with iodine to yield a diene. The nickel catalysed carbozincation of alkynes has been combined with an iodine work-up to provide access to vinylic iodides (Scheme 27).[54] Transition metals are normally employed to prevent propargylic (prop-2-ynylic) halides isomerising to the corresponding allenes. However, this transformation has been put to good use for the preparation of 2-iodobuta-1,3-diene derivatives (Scheme 28).[55] Reaction of the propargylic bromide with the Grignard reagent gave the allene which was reacted with iodine to produce the desired compounds.



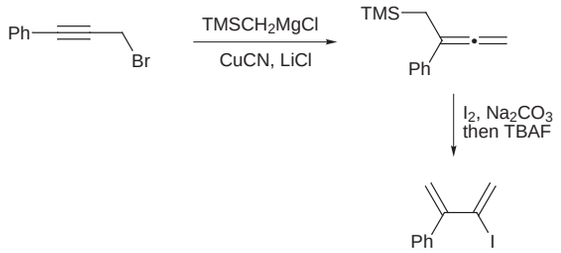
Scheme 25



Scheme 26



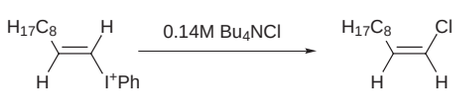
Scheme 27



Scheme 28

3.2 From other vinyl derivatives

A synthesis of (fluorovinyl)trimethylsilanes from the electrochemical silylation of fluoroalkenes has been reported.[56] Two related papers have published routes to fluoro-substituted alkenes and dienes from a palladium coupling reaction of vinylstannanes. A palladium and copper halide co-catalysed stereospecific coupling of 1-fluorovinylstannanes with aryl iodides or acyl chlorides gave tetra-substituted fluoroalkenes.[57] On a similar note, the same catalyst combination has been employed to produce difluoro substituted dienes.[58] Okuyama *et al*. have reported what they term a vinylic S_N2 reaction of dec-1-enyliodonium salts with halide ions to produce haloalkenes (Scheme 29).[59]



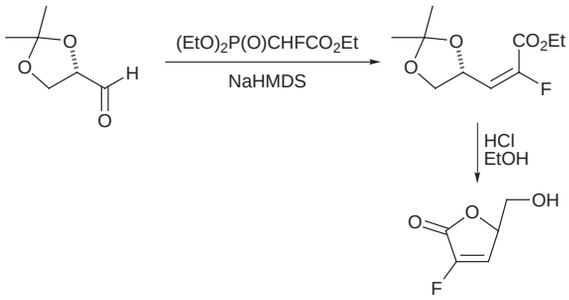
Scheme 29

3.3 By C=C bond formation

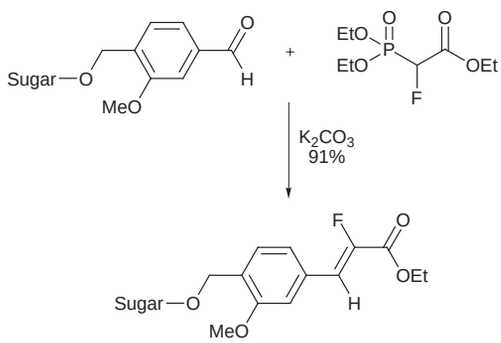
The synthesis and desaturation of monofluorinated fatty acids has been reported.[60] Halogenated Horner–Wadsworth–Emmons reagents have been utilised to form fluoroalkenes. The synthesis of fluoro substituted purine nucleosides (Scheme 30)[61] and inhibitors of lignin polymerisation (Scheme 31)[62] have both been achieved in this way. On a similar note, an efficient synthesis of fluoro derivatives of diphosphonates, and their reaction with aldehydes to give vinyl phosphonates has been reported.[63] Reaction of β-fluorovinamidinium salts with activated methylene compounds has been studied.[64] The production of functionalised alkenes, and in particular, bromo derivatives, has been achieved by elimination over solid supports under microwave irradiation.[65]

3.4 By other methods

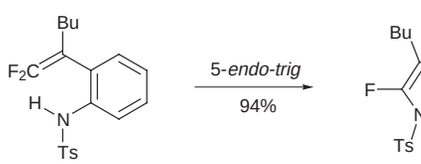
The reactions and kinetics of benzylfluorocarbene have been assessed and used to provide routes to vinyl fluorides.[66] The



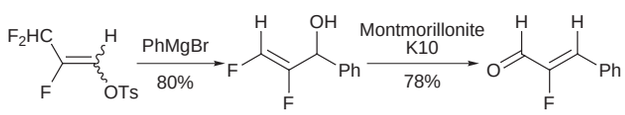
Scheme 30



Scheme 31

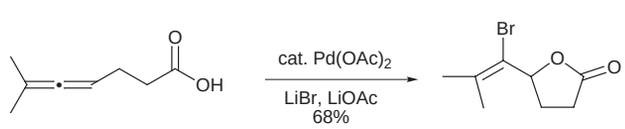


Scheme 32



Scheme 33

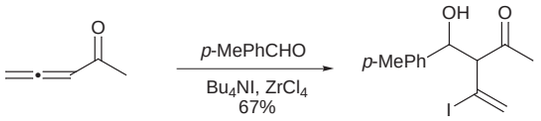
synthesis of 2-fluorinated indoles and related compounds has been achieved *via* a 5-*endo-trig* cyclisation (Scheme 32).[67] The reaction of Grignard reagents with propenyl toluene-*p*-sulfonates has provided routes to α-fluoro-α,β-unsaturated aldehydes in a highly efficient and stereoselective manner (Scheme 33).[68] The use of allenes to access vinyl halides has been notable this year. Jonasson and Bäckvall have introduced a palladium catalysed intramolecular 1,2 oxidation of allenes[69] (Scheme 34) and Zhang and Lu have highlighted a convenient synthesis of iodo substituted homoallylic alcohols[70] (Scheme 35). As a key step towards bridge-methylated decalins, Janda and co-workers have utilised a phosphorus tribromide mediated S_N2' bromination of an allylic alcohol (Scheme 36).[71] Finally, two α-iodinations of carbonyl compounds: reaction of enaminones with bis(pyridine)iodinium tetrafluoroborate has been reported[72] as has the functionalisation of ketones with iodine mediated with bis(tetrabutylamine) peroxydisulfate.[73]



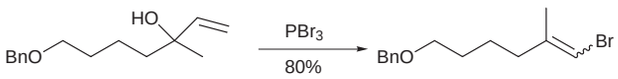
Scheme 34

4 Aryl halides

Electrophilic fluorination of fluoroaromatics has been reported to proceed using trifluoromethanesulfonic acid and trichloro-

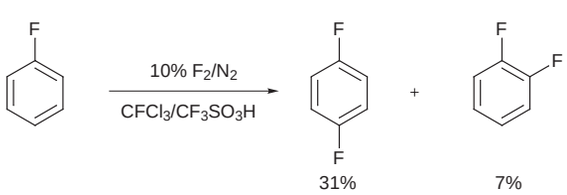


Scheme 35

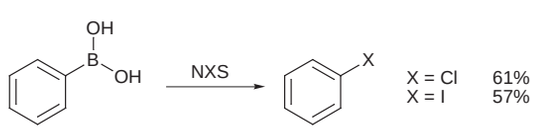


Scheme 36

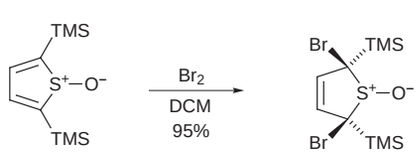
fluoromethane as the solvent (Scheme 37).[74] Fluorinated quinolines have been prepared and functionalised by reaction with organolithium reagents.[75] Fluoro-substituted *O*-glucuronides have been synthesised and their intrinsic and intramolecular lipophilicity effects studied.[76] A mild preparation of haloarenes has been published which involves *ipso* substitution of arylboronic acids with *N*-halosuccinimides (Scheme 38).[77] Dibromothiophene has been synthesised *via* an exclusive *cis*-1,4-addition reaction.[78] Bromination of 2,5-bis(trimethylsilyl)-thiophene monoxide proceeds as laid out in Scheme 39. By supporting zinc bromide on a solid, a fast and selective bromination of aromatic substrates has been achieved.[79] Direct bromination and halogen exchange reactions on phenanthrolines have been reported giving access to symmetrical and unsymmetrical dihalo derivatives (Scheme 40).[80] Site selective substitution of 2-chloro-6-trifluoromethylpyridine has been termed a "halogenshuffle" by Schlosser and co-workers.[81] Effective iodination of aromatic compounds has been achieved by simple means in the last year. A room temperature regioselective iodination of aromatic ethers mediated by Select-Fluor® has been reported,[82] as has an efficient regioselective direct iodination using iodine and nitrogen dioxide.[83]



Scheme 37



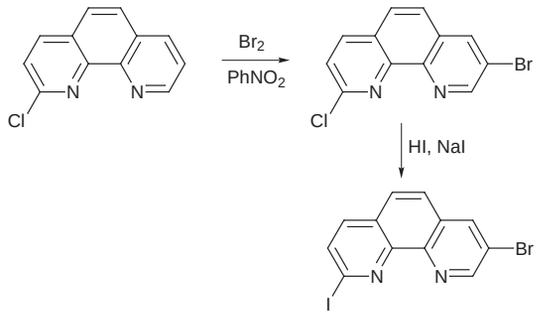
Scheme 38



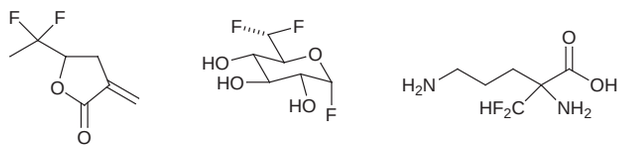
Scheme 39

5 1,1-Dihalo and related compounds

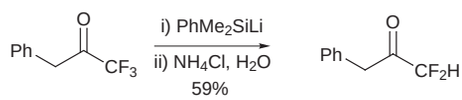
The preparation of dihalo compounds has seen significant progress in the past year, particularly *gem*-difluorides. Of interest for biological testing are the preparation of α-methylene-γ-butyrolactones with difluoromethylene functionalities, **5**,[84] 6-deoxy-6,6-difluoroglucopyranosides, **6**,[85] and fluorinated derivatives of ornithine, **7**.[86] Fleming has reported a procedure to obtain *gem*-α-difluorides from trifluoromethylated ketones (Scheme 41).[87] Using phenyldimethylsilyllithium the intermediate enol is trapped. This can then be used in aldol reactions, or simply quenched to give the desired product. A similar reductive defluorination has been achieved by electrochemical means, to



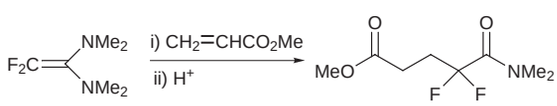
Scheme 40



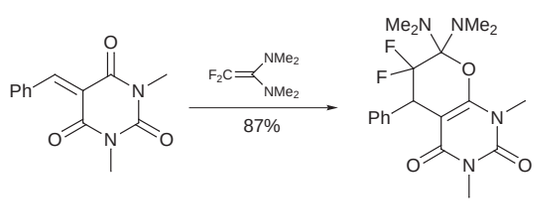
5 **6** **7**



Scheme 41

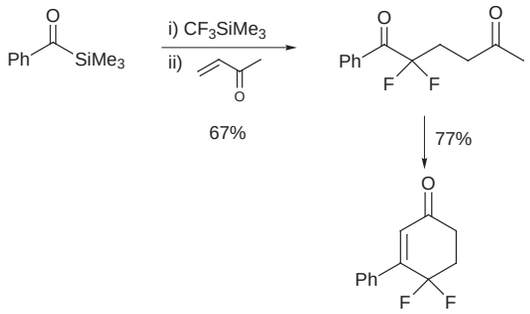


Scheme 42

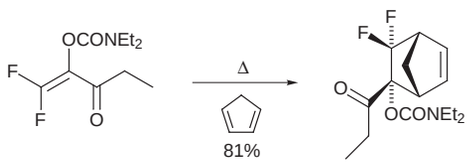


Scheme 43

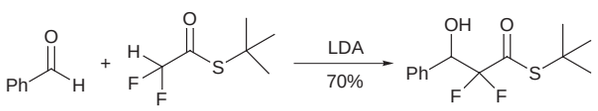
produce difluorinated silyl enol ethers in good yield.[88] Xu and Dolbier have used 1,1-bis(dimethylamino)-2,2-difluoro ethene to produce *gem*-difluoro amides (Scheme 42).[89] This reagent adds in a Michael fashion to α,β-unsaturated aldehydes, ketones and esters. The same reagent has also been applied to the synthesis of novel fluorinated derivatives of barbituric acid by a hetero Diels–Alder reaction (Scheme 43).[90] Fluorinated enamines have also been made by electrochemical means, then used to give difluorinated organic compounds in good yield.[91] Trimethylsilyl ketones have also been used to provide access to *gem*-difluorinated ketones (Scheme 44).[92] The Diels–Alder reactivity of difluoroalkene dienophiles has been assessed by Percy and co-workers (Scheme 45).[93] The preparation of difluoro ketones and related compounds has seen increased use through carbon–carbon bond formation on the fluorine substituted α-carbon. Weigel has published a route to α,α-difluoro hydroxy thioesters through enolization of the precursor thioester (Scheme 46).[94] In a similar manner, a magnesium promoted synthesis of homoallylic alcohols from allylic *gem*-difluorides has been noted.[95] The same bond construction, but using radical assembly has also been employed. Generation and intramolecular cyclisation of difluoroalkyl radicals *via* single electron transfer from a benzeneselenolate anion has led to the synthesis of difluoro-γ-lactones (Scheme 47).[96] Both enantiomers of α,α-difluoro alanolide have been synthesised by a similar route, but using tributyltin as the radical initiator.[97] The generation and reactions of difluorocyclopropyl anion have been the subject of interest.[98] Reaction of cyclic alkenes



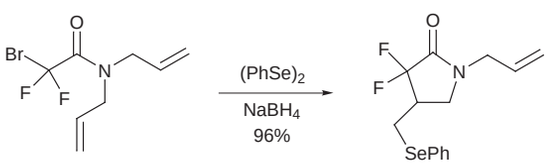
Scheme 44



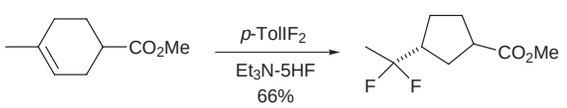
Scheme 45



Scheme 46



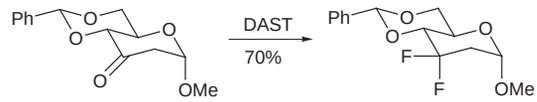
Scheme 47



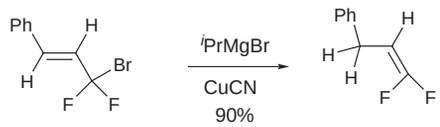
Scheme 48

Scheme 49

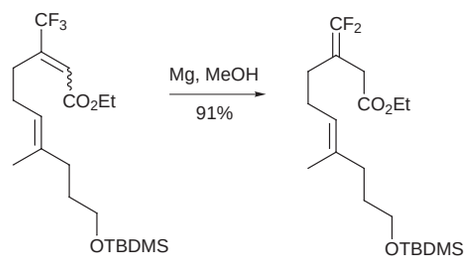
with *p*-iodotoluene difluoride has been shown to result in a ring contraction (Scheme 48).[99] A new expedient route to the stereoselective synthesis of fluorinated diol derivatives *via* aluminium acetals has been published.[100] The use of DAST to transform ketones to their difluoro derivatives continues to be of synthetic value. The potentially sensitive ketal functional group was not affected during the transformation laid out in Scheme 49.[101] A similar reaction was performed during the synthesis of gemcitabine (Scheme 50).[102] Synthetically useful difluorophosphonates have been prepared by electrophilic fluorination of α-carbanions of benzylic phosphonates with *N*-fluorobenzenesulfonamide.[103] Two routes to 1,1-difluoroalkenes have been reported this year. Michael addition to allylic fluorides proceeded with loss of a bromide to give the desired products (Scheme 51).[104] An alternative approach is outlined in Scheme 52. Fluoride elimination from a β-anionic intermediate was used in the synthesis of a cannabinoid ligand.[105] Difluorostyrene derivatives have been synthesised by coupling of 2,2-difluoro-1-iodoethene with appropriate benzenoid compounds.[106] A similar coupling approach has also resulted in the production of iododifluorostyrenes.[107] A convenient synthesis



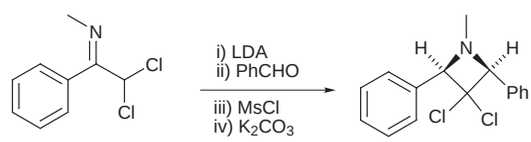
Scheme 50



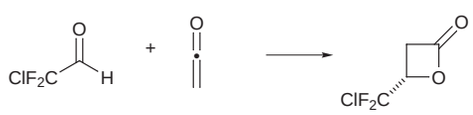
Scheme 51



Scheme 52

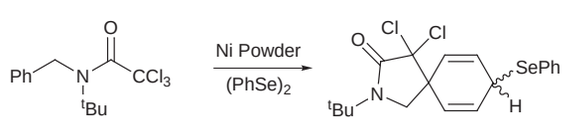


Scheme 53

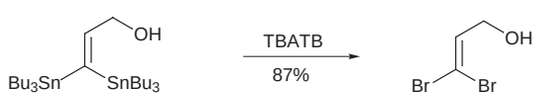


Scheme 54

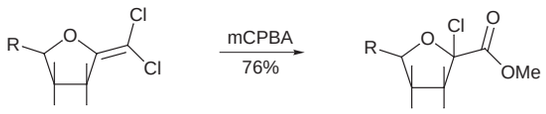
of a series of 3,3-dichloroazetidines has been published (Scheme 53).[108] Dichloroalkenes have been prepared by a Ramberg–Bäcklund rearrangement of trichlorosulfones.[109] The chiral building block (*S*)-β-chlorodifluoromethyl-β-propiolactone has been prepared by a [2 + 2] cycloaddition process (Scheme 54).[110] Dichloro substituted spirolactams have been synthesised by a novel *ipso* radical cyclisation which results in loss of aromaticity from the cyclising group (Scheme 55).[111] The deacetylation of dibromoacetoacetates with lithium percholate has produced a route to bromo substituted esters.[112] Quayle and co-workers have continued their investigation into bis-stannyl ethenes.[113] Reaction with tetra-*n*-butylammonium tribromide (TBATB) gives the corresponding bromo derivatives (Scheme 56). Treatment of dichloroalkenes with MCPBA results in the oxidative incorporation of chloride (Scheme 57). This has been used in a short synthesis of α-azido ulosonic esters.[114] Finally, the electrolytic partial fluorination of oxoindole and benzothiazolyl sulfides has been the subject of some study.[115,116]



Scheme 55



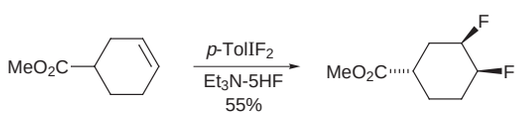
Scheme 56



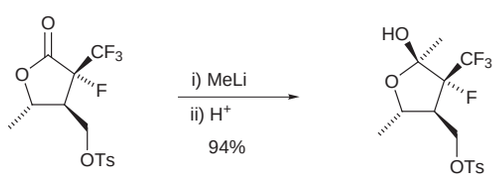
Scheme 57

6 1,2-Dihalo compounds and 1,2-halohydrins

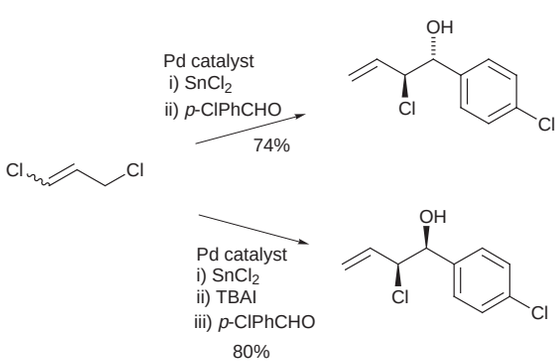
The volume of work on 1,2-dihalo compounds and 1,2-halohydrins warrants that these two sections are combined this year. The difluorination of alkenes with iodotoluene difluoride has been reported (Scheme 58).[117] The stereocontrolled production of a fluorohydrin has been shown from a novel nucleophilic addition to fluorinated lactones (Scheme 59).[118] Fluorinated sugar analogues continue to be an area of interest. The asymmetric synthesis of fluorinated pyranose derivatives has been noted,[119] as has an approach to fluorinated glycosides using SelectFluor®.[120] The use of manganese chloride under an oxygen atmosphere has been used to access dichloro compounds from the corresponding alkenes.[121] A selective *syn* or *anti* addition of allyl nucleophiles to aldehydes has been achieved with palladium and tin organometallic reagents (Scheme 60).[122] The use of tetrabutylammonium salts determined the reversal of selectivity. O'Neil and co-workers have used homochiral amine *N*-oxides to induce asymmetric reduction of α-chloro ketones to produce 1,2-chlorohydrins (Scheme 61).[123] During the enantiospecific synthesis of (+)-2-pupukeanone, a regioselective hydrobromination with NBS was employed (Scheme 62).[124] A similar protocol has been used for the synthesis of unsaturated oxaspiropentanes.[125] Finally, Sweeney has used an iterative hydroxyiodination of acetoxycyclohexenes to provide a concise route to conduritol derivatives (Scheme 63).[126]



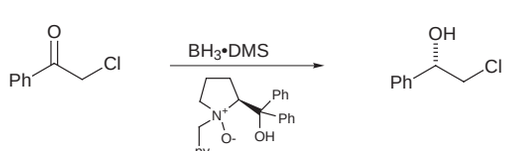
Scheme 58



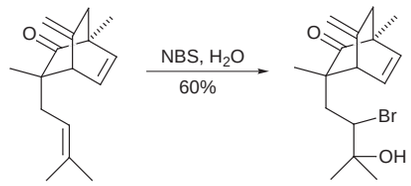
Scheme 59



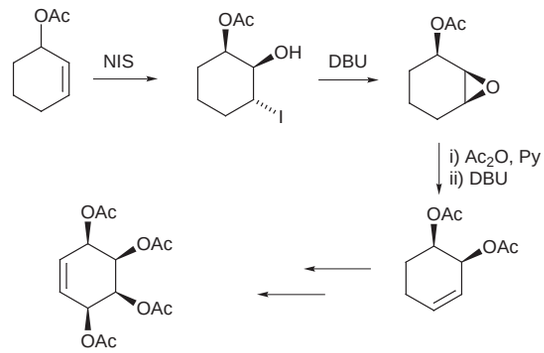
Scheme 60



Scheme 61



Scheme 62

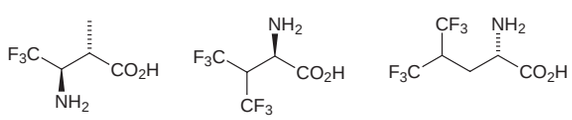


Scheme 63

7 Trifluoromethyl compounds

The use of the trifluoromethyl group in organic synthesis continues to grow. This section was added in last year's review to reflect this area of chemistry, and is maintained this year. It is not an exhaustive account, but will highlight important advances and methodologies which will be of interest to organic chemists.

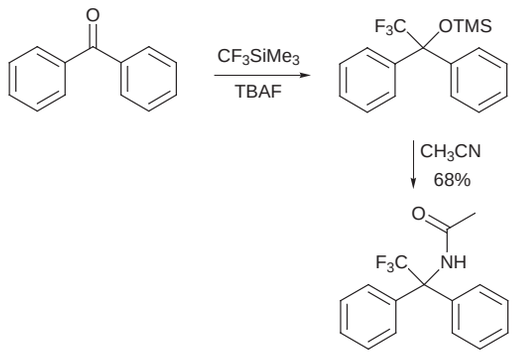
One important area which has seen some activity this year is trifluoromethyl substituted amino acids. Stereochemically defined α-alkyl-β-fluoroalkyl-β-amino acids, such as **8** have been produced by biomimetic transaminations from the corresponding β-keto esters.[127] Asymmetric syntheses of hexafluorovaline, **9**, and hexafluoroleucine, **10**, have been reported.[128,129] Of structural and reactivity interest, the stable enol 2,2-bis(trifluoromethylthio)ethanol has been synthesised and studied.[130] The synthesis of new glycopeptide motifs has been achieved by the glycosylation of 2-(trifluoromethyl)-aspargine.[131] Van Der Puy has prepared bis(trifluoromethyl) substituted compounds *via* functionalisation of octafluoropentane.[132] The trifluoromethyl group has been used as a sensitive NMR probe for remote diastereotopicity in second generation trifluoromethyl substituted chiral dendrimers.[133]



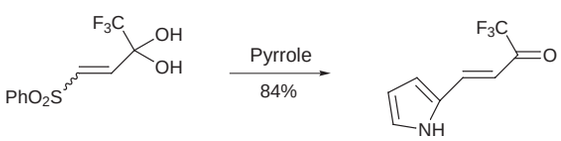
8 **9** **10**

The use of fluoroform as an efficient precursor for the trifluoromethylation of aldehydes has been reported (Scheme 64).[134] Reaction with dimethylsulfonium anion produces the trifluoromethyl anion which reacts with carbonyl compounds. The use of microbial or enzymatic methodology and the influence of substituents continues to be an area of interest. Two papers have reported on the relative abilities of methyl and trifluoromethyl groups to direct an enantioselective reduction of carbonyl groups.[135,136] A one pot preparation of trifluoromethyl amides from ketones by reaction with (trifluoromethyl)-trimethylsilane has been noted (Scheme 65).[137] An efficient synthesis of heteroaryl substituted α,β-unsaturated trifluoromethyl ketones has been reported (Scheme 66).[138] Initial Michael addition is followed by loss of the phenylsulfonyl group to reform the unsaturation. The chemoselective trifluoromethylation of methyl esters using germanium organometallic reagents has

Scheme 64

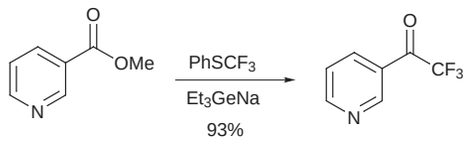


Scheme 65

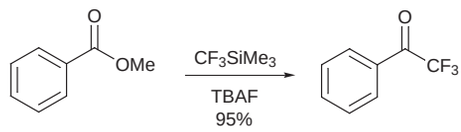


Scheme 66

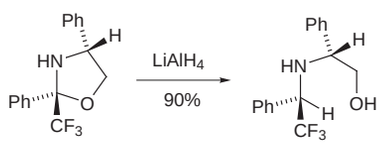
been used to provide an efficient synthesis of trifluoromethyl ketones (Scheme 67).[139] A similar overall transformation has also been achieved with (trifluoromethyl)trimethylsilane and TBAF (Scheme 68).[140] The preparation of 3,3,3-trifluoropropiondithioacetals as CF_3-containing building blocks has been reported.[141] The asymmetric synthesis of substituted trifluoroethylamines has been achieved through a stereospecific reduction of fluoral derived oxazolidines (Scheme 69).[142] An efficient preparation of trifluoromethyl substituted aryl acroleins has been presented.[143] A concise stereoselective synthesis of fluoro substituted alkyl amines has been achieved *via* the addition of *N*-lithiated amines to enol ethers followed by subsequent metalation and quenching with an aldehyde to form new functionalised enamines (Scheme 70).[144] The same group have also reported on a stereoselective route to hindered β-ethoxy allylic alcohols and crotonates using trifluoromethyl ethoxy vinyl anions.[145] Trifluoromethyl substituted olefins have been accessed by a palladium mediated coupling with terminal alkynes.[146] Highly stereoselective S_N2' reactions of Grignard reagents have been examined based on attack on trifluoromethyl allylic acetates (Scheme 71).[147] Novel reactions of allylic alcohols with hexafluoropropene–diethylamine adduct lead to a trifluoro substituted amide species which could be elaborated to a γ-lactone *via* a [3,3] sigmatropic rearrangement (Scheme 72).[148] Hiraoka *et al*. have reported a highly regio- and stereoselective alkyl substitution with copper reagents for the construction of chiral trifluoromethyl quaternary carbon centres.[149] A [2 + 2] cycloaddition has been utilised in the diastereoselective preparation of β-lactams (Scheme 73).[150] A new convenient route for the trifluoromethylation of steroidal molecules has been published.[151] Lewis acid promoted cross coupling of trifluoromethyl acetals with trimethylsilyl enol ethers has been used to give appropriately substituted fluorine compounds.[151] The synthesis of optically active trifluoromethyl substituted aziridines has been achieved *via* an intramolecular S_N2 reaction as laid out in Scheme 74.[153] A novel preparation of trifluoromethyl substituted isoserine derivatives has also been reported,[154] as has the synthesis of a pyroglutamic acid.[155] Okadu *et al*. have achieved a convenient synthesis of a fluorine containing azepine by a thermally induced cyclisation reaction



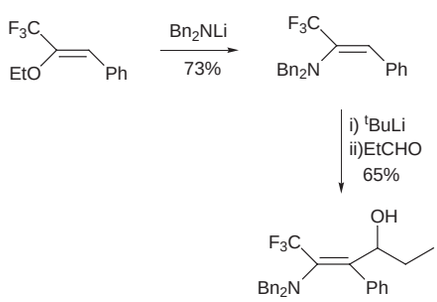
Scheme 67



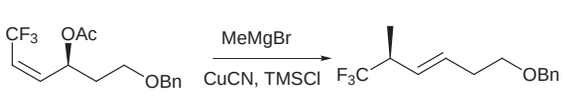
Scheme 68



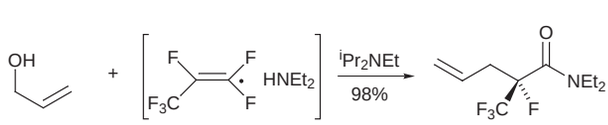
Scheme 69



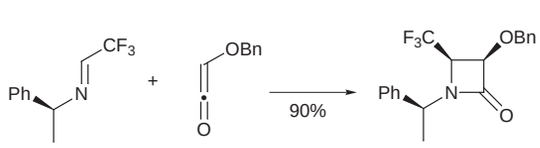
Scheme 70



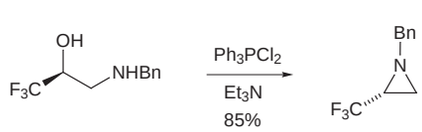
Scheme 71



Scheme 72

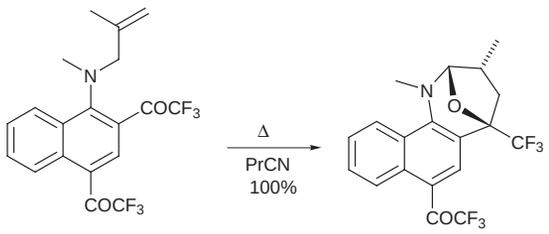


Scheme 73

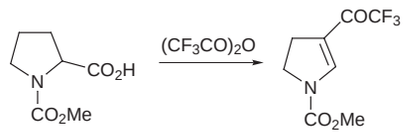


Scheme 74

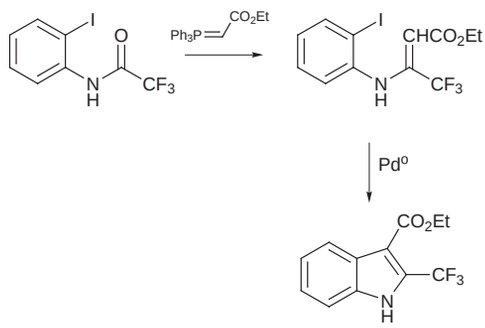
(Scheme 75).[156] A study of the flash vacuum pyrolysis of trifluoromethyl substituted diazomethanes, has been published.[157] An anomalous Dakin–West reaction has been used to prepare trifluoroacetyl substituted pyrrolidine compounds (Scheme 76).[158] By using sequential Wittig and Heck reactions, Latham and Stanforth have achieved an efficient synthesis of indoles and quinolines (Scheme 77).[159] Another convenient preparation of fluoro substituted quinolines has been highlighted.[160] The optical resolution and asymmetric synthesis of a trifluoro-



Scheme 75

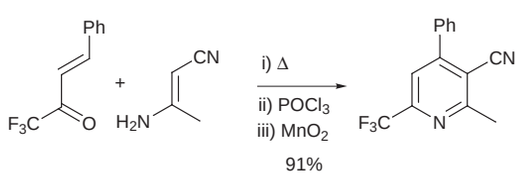


Scheme 76



Scheme 77

methyl substituted pyrrole derivative has been reported.[161] The preparation of trifluoromethyl substituted pyridines has been the subject of some interest this year. A convenient synthesis of 6-substituted pyridines has been reported (Scheme 78).[162] Two related preparations of similar compounds are also noted by Okada *et al*.[163] and the 4-substituted compounds have been noted by Katsuyama *et al*.[164] Finally, trifluoromethyl substituted pyrazole and triazine compounds have been prepared by regioselective reaction of oxazolium anions.[165]



Scheme 78

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