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Application of *N*-Halo Reagents in Organic Synthesis

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This review article summarizes published data on the application of *N*-halo reagents (such as *N*-halo amines, *N*-halo amides and/or imides, *N*-halo sulfonamides and/or imides, and *etc*.) in various organic functional group transformations such as: oxidation reactions, deprotection and protection of different functional groups, halogenation of saturated and unsaturated compounds, acylation of alcohols, phenols, amines or thiols, epoxidation of alkenes, aziridination and *etc*. The main purpose of writing this review is encouraging of active researchers interested to this field for the synthesis of new *N*-halo reagents specially with different halogens and applications of these new *N*-halo reagents in organic reactions or finding more and more applications of existing *N*-halo reagents in organic synthesis.

Keywords: *N*-Halo reagents, *N*-Halo imides, *N*-Halo amines, *N*-Halo sulfonamides, *N*-Halo amides, *N*-Halo sulfonimides

This article is dedicated to Professor Seyyed Ahmad Banihashemi one of the founders of polymer chemistry in Iran on the occasion of his 75th birthday.

INTRODUCTION

Synthetic methodology, as the building block of organic synthesis, continuously seeks for new reagents, better reaction conditions, and more efficient and selective methods. In this regard, a large group of compounds entitled *N*-halo reagents are widely used in fine organic synthesis. These include *N*-halo derivatives of amines, amides, imides, urea, saccharines, sulfonamides, sulfonimides, and *etc*. Although the scope of the application of such compounds is so wide that all *N*-halo reagents can not be considered within the framework of a single review article, but we decide to introduce them briefly and believe that it may be useful to achieve new idea and applications. In the other way, the chemistry of *N*-halo reagents was the subject of several review articles [1-8]. However, since that time numerous new data has been appeared in the literature which are summarized in the present review. Some specific features of *N*-halo reagents such as high activity of the *N*-X bond and various modes of its splitting, determine their wide application in organic synthesis.

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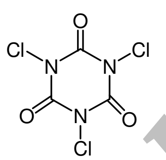
Depending on the conditions, a number of highly reactive intermediates can be formed including halogen radicals, halogen cations, halogen anions, *N*-radicals, *N*-cations, *N*-anions, *etc*. Consequently, *N*-halo reagents have the potential to promote important reactions such as halogenation, oxidation, and protection as well as formation of C-X, C-O, and C=O bonds. In addition to the numerous organic and inorganic halogenating agents, *N*-halo reagents play an especially important role in the chemistry of natural compounds. Some of the *N*-halo reagents which are presented in Tables 1-4 are reviewed in this article.

TRICHLOROISOCYANURIC ACID

Trichloroisocyanuric acid (TCCA, **1**), 1,3,5-trichloro-1,3,5-triazine-2,4,6-(1*H*, 3*H*, 5*H*)-trione, was first synthesised in 1902 from the reaction of the potassium salt of cyauric acid with chlorine gas [9]. TCCA was commonly named as Symclosene, ACL-85 and Chloral [10,11].



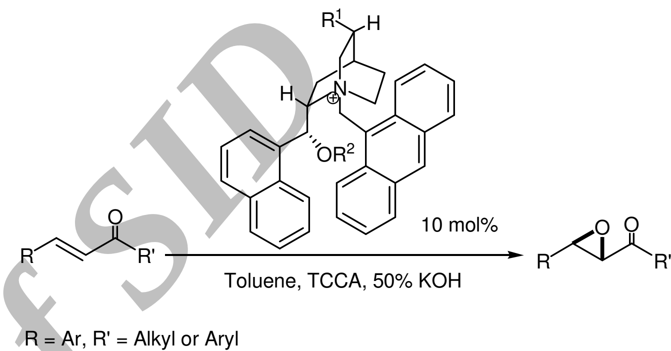
1

The worldwide production of TCCA is considerably increased for its purpose as disinfecting swimming pools, cleaning and sterilizing bathrooms and using in laundry. Recently, TCCA has found many uses in organic synthesis. The application of TCCA in organic transformations was reviewed in 2002 extensively by Tilstam and Wienmann [12]. Herein the application of TCCA in organic synthesis is reviewed from that time.

Oxidation Reactions

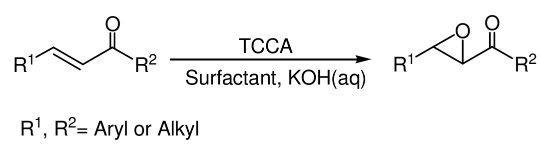
Oxidations by TCCA are mainly categorized into two sections, transfer of oxygen and dehydrogenation. An interesting application of TCCA is the conversion of α,β-unsaturated carbonyl compounds to their corresponding epoxides. TCCA has been used for the oxidation of enones in few hours under mild conditions [13].

The enantioselective epoxidation of chalcones was carried out using TCCA as oxidant in the presence of a chiral quaternary ammonium salt as a phase transfer catalyst in good yields with moderate enantiomeric excesses (Scheme 1) [14].



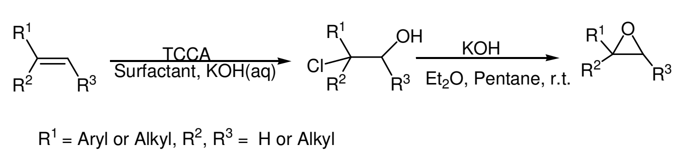
Scheme 1

TCCA was used in the presence of base as an efficient oxidant for the epoxidation of enones and tandem oxidation-epoxidation of allylic alcohols in a water suspension system in the presence of a surfactant (Scheme 2) [15].



Scheme 2

The preparation of epoxides was efficiently achieved by the reaction of alkenes with TCCA in aqueous acetone followed by treatment of the resulting chlorohydrin with aqueous KOH in ether/pentane (Scheme 3) [16].



Scheme 3

Table 1. The Name and Structure of *N*-Bromo Reagents

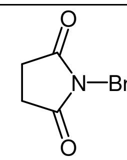
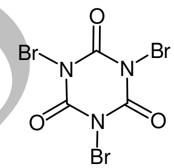
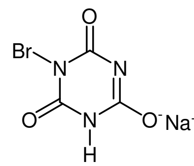
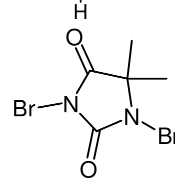
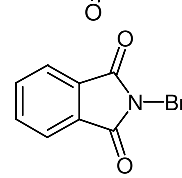
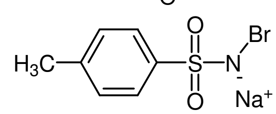
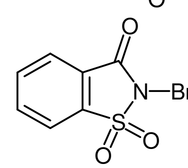
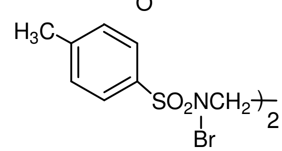
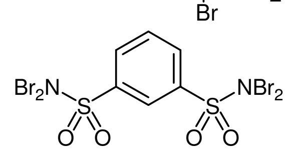
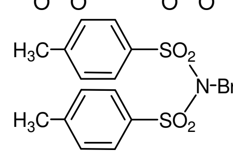
Name	Abbreviate name	Structure
N-Bromosuccinimide	NBS	
Tribromoisocyanuric acid	TBCA	
Sodium monobromo isocyanurate	SMBI	
1,3-Dibromo-5,5-dimethylhydantoin	DBDMH, DBH	
N-Bromophthalimide	NBPI	
N-Bromo-*p*-toluenesulfonamide sodium salt (Bromoamine T)	-	
N-Bromosaccharin	NBSa	
N,N′-Dibromo-*N,N′*-1,2-ethanediyl -bis (*p*-toluenesulfonamide)	BNBTS	
N,N,N′,N′-Tetrabromobenzene-1,3-disulfonamide	TBBDA	
N-Bromo bis(*p*-toluenesulfonyl)amine	NBBTA	

Table 1. Continued

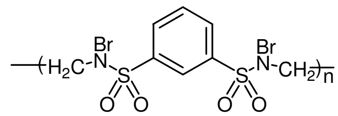
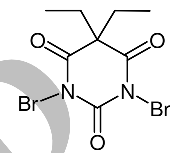
Poly *N*-bromo benzene-1,3-sulfonamide	PBBS	
1,3-Dibromo-5,5-diethylbarbituric acid	-	

Table 2. The Name and Structure of *N*-Chloro Reagents

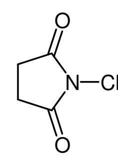
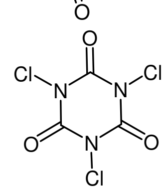
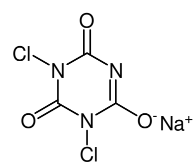
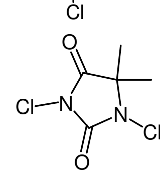
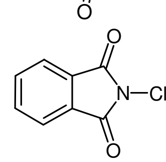
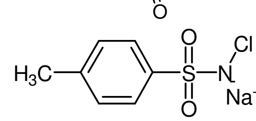
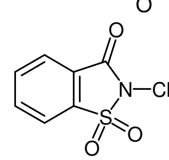
Name	Abbreviate name	Structure
N -Chlorosuccinimide	NCS	
Trichloroisocyanuric acid	TCCA	
Sodium dichloroisocyanurate	SDCI	
1,3-Dichloro-5,5-dimethyl hydantoin	DCDMH, DCH	
N -Chlorophthalimide	NCPI	
N-Chloro-*p*-toluenesulfonamide sodium salt (Chloramine T)	-	
N -Chlorosaccharin	NCSac	

Table 2. Continued

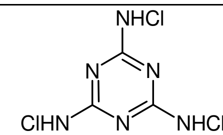
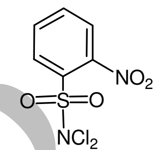
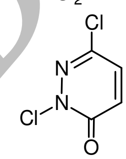
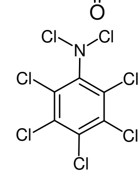
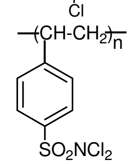
Trichloromelamine	TCM	
2-Nitro-*N,N′*-dichloro-benzensulfonamide	2-$NsNCl_2$	
2,6-Dichloropyridazin-3(2H)-one	-	
N,N,2,3,4,5,6-Heptachloroaniline	-	
Poly[4-vinyl-*N,N′*-dichlorobenzenesulfonamide]	-	

Table 3. The Name and Structure of *N*-Flouro Reagents

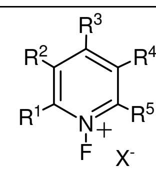
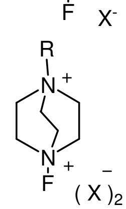
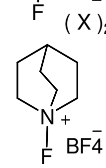
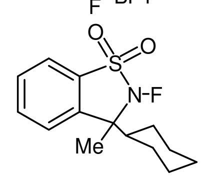
Name	Abbreviate name	Structure
N-Flouropyridinium salts	-	
1-Alkyl-4-fluro-1,4-diazabicyclo [2,2,2]octane	-	
N-Fluoroquinuclidinium tetrafluoroborate	-	
N-Fluoro-3-cyclohexyl-3-methyl-2,3-dihydrobenzo[1,2-d]isothiazole-1,1-dioxide	CMIT-F	

Table 3. Continued

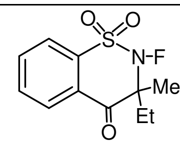
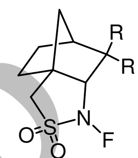
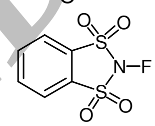
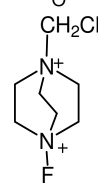
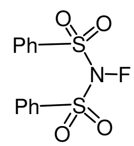
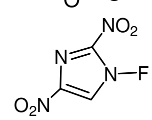
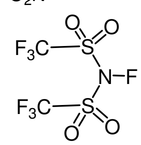
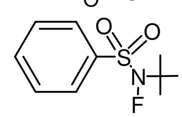
N-Fluoro-3-ethyl-3-methyl-1,1-dioxo-2,3-dihydro-1λ^6-benzo[e]1,2-thiazin-4-one	-	
N-Fluorocamphorsultam	-	
N-Fluoro-*o*-benzenedisulfonimide	NFOBS	
1-(Chloromethyl)-4-fluoro-1,4-diazabicyclo [2,2,2]octane bis(tetrafluoroborate)	F-TEDA-BF_4	
N-Fluorobenzensulfonimide	NFSi	
N-Flouro-2,4-dinitroimidazole	NF-2,4-DNI	
N-Flouro bis[(trifluoromethyl)sulfonyl]imide	-	
N-*t*-Butyl-N-flurobenzensulfonamide	-	

Table 4. The Name and Structure of *N*-Iodo Reagents

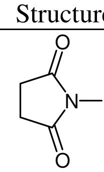
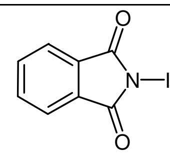
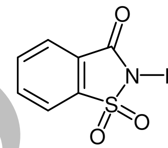
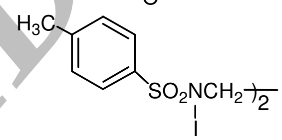
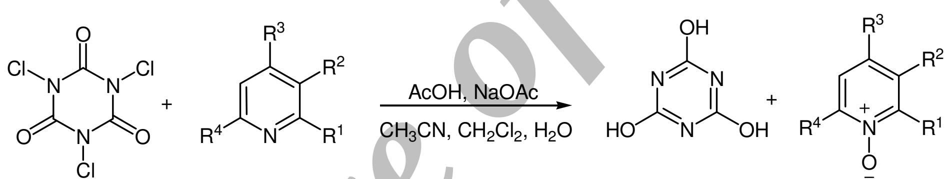
Name	Abbreviate name	Structure
N-Iodosuccinimide	NIS	

Table 4. Continued

N-Iodophthalimide	NIPI	
N-Iodosaccharin	NISac	
N,N′-Dibromo-*N,N′*-1,2-ethanediylbis(*p*-toluenesulfonamide)	BNITS	

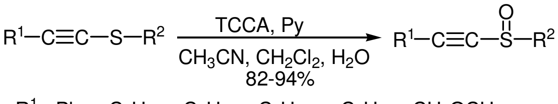


R^1 = H, Methyl, Vinyl, Cl, R^2 = H, Methyl, Vinyl
R^3 = H, Methyl, Vinyl, R^4 = H, Methyl

Scheme 4

Oxygen transfer to nitrogen was also achieved by TCCA. Pyridine and its derivatives were readily oxidized to their *N*-oxides with a solution of TCCA, acetic acid, sodium acetate and water in acetonitrile and dichloromethane with 78-90% yields (Scheme 4) [17].

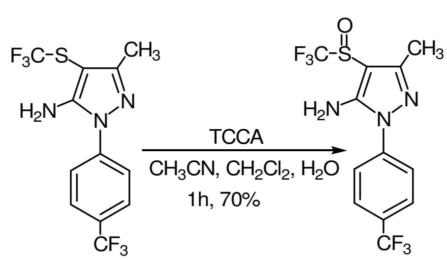
Acetylenic sulfides were oxidized to acetylenic sulfoxides by a solution of pyridine, water, benzoic acid and TCCA in acetonitrile and dichloromethane (Scheme 5) [18].



R^1 =Ph, n-C_3H_7, n-C_4H_9, n-C_6H_{13}, n-C_5H_{11}, -CH_2OCH_3
R^2 = Ph, 4-MeC_6H_4

Scheme 5

TCCA was successfully used for the synthesis of Fipronil **2** (a highly efficient insecticide) from the corresponding sulfide (Scheme 6) [19].



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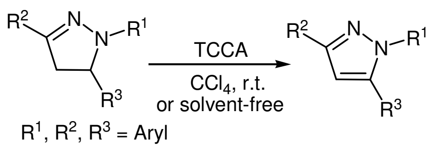
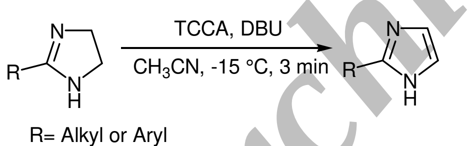
Scheme 6

The second oxidation mechanism by TCCA involves dehydrogenation. This behavior may be applied for the aromatization of cyclic compounds or oxidation of alcohols, primary amines and hydrazines. TCCA was used for the oxidation of 1,3,5-trisubstituted pyrazolines to their corresponding pyrazoles under either heterogeneous or solvent-free conditions in good yields at room temperature (Scheme 7) [20].



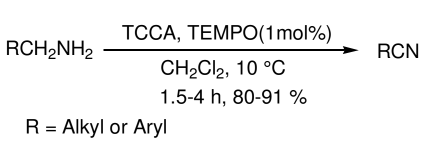
Scheme 7

Similar reactions were carried out under microwave irradiation in acetic acid [21]. Dehydrogenation of a variety of 2-imidazolines to the corresponding imidazoles was achieved by TCCA in the presence of DBU (Scheme 8) [22]. Chemoselective oxidation of these compounds was successfully carried out in the presence of sulfides and alcohols.



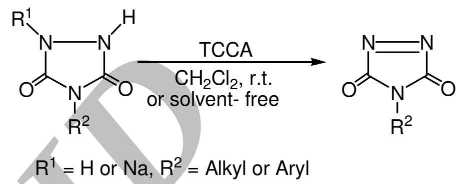
Scheme 8

Chen and his co-workers reported the oxidation of primary amines into nitriles by TCCA in the presence of a catalytic amount of TEMPO under mild reaction conditions (Scheme 9) [23]. Optimization of the reaction condition showed that the best results were obtained in dichloromethane at 10 ºC and the use of 1 mol% of the catalyst.



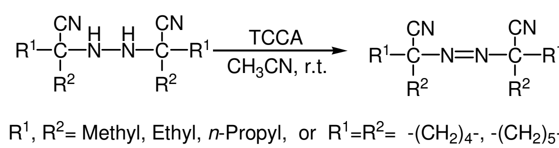
Scheme 9

TCCA was used for the oxidation of urazoles and bis-urazoles to their triazolinediones under both heterogeneous and also solvent-free conditions with excellent yields at room temperature (Scheme 10) [24].



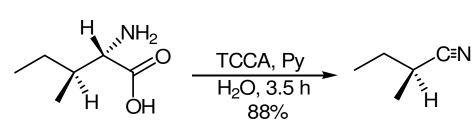
Scheme 10

Dehydrogenation of 1,2-bis(cyanoalkyl)hydrazines for the synthesis of azobisnitriles was reported by Mohite, *et al.* by the use of TCCA in acetonitrile at room temperature (Scheme 11) [25]. Azobisnitriles are an important class of compounds that are widely used as initiators in free radical polymerization reactions.



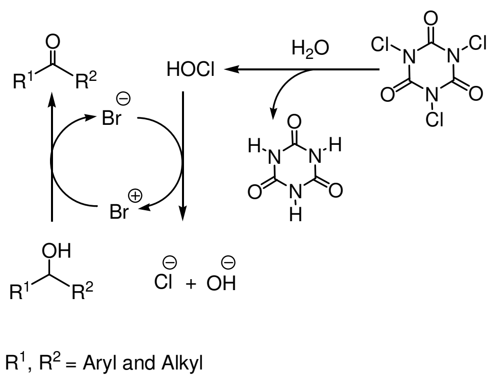
Scheme 11

An interesting application of TCCA was reported by Hieagl, *et al.* in the conversion of α-aminoacids into nitriles by oxidative decarboxylation in water or methanol in the presence of pyridine [26]. For example L-isoleucine was converted to (S)-(+)-2-methylbutyronitrile in 88% yield after 3.5 h with no considerable loss of its optical purity (Scheme 12).



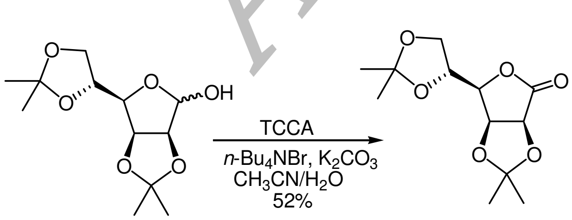
Scheme 12

TCCA takes part in dehydrogenation of primary and secondary alcohols for their conversion to aldehydes and ketones, respectively. Chemoselective oxidation of benzylic and secondary alcohols was achieved by the use of TCCA and wet SiO_2 in the presence of a catalytic amount of KBr under heterogeneous conditions at room temperature (Scheme 13) [27].



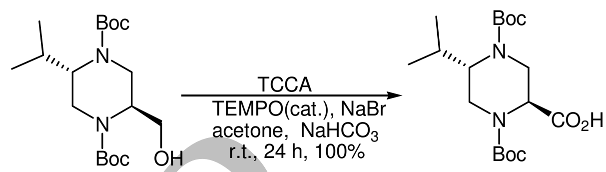
Scheme 13

In some examples TCCA has been used for the oxidation of primary alcohols to carboxylic acids. For instance, by the combined use of catalytic $RuCl_3$ (1.0 mol%) and stochiometric amount of TCCA in the presence of *n*-Bu_4NBr and K_2CO_3, smooth oxidation of primary alcohols to carboxylic acids was occurred [28]. Secondary alcohols were oxidized to ketones using a similar set of reagents. The method is mild and permits the chemoselective oxidation of alcohols in the presence of other sensitive functional groups such as vinyl and ketals (Scheme 14).

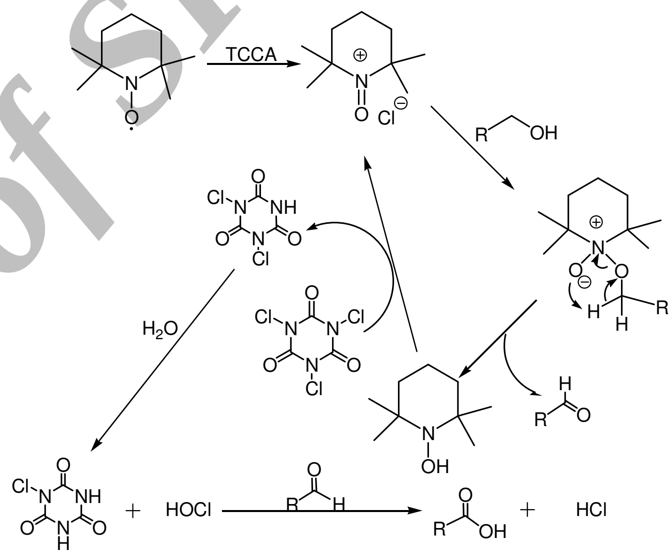


Scheme 14

Efficient oxidation of primary alcohols to the corresponding carboxylic acids was carried out at room temperature and in acetone/water, using TCCA in the presence of a catalytic amount of TEMPO [29]. The mild conditions of procedure and the total absence of any transition metal make the reaction suitable for safe laboratory use (Scheme 15). A mechanism was proposed for these reactions (Scheme 16).

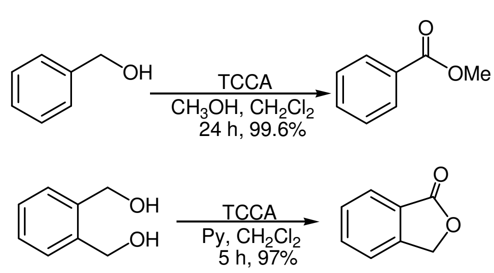


Scheme 15



Scheme 16

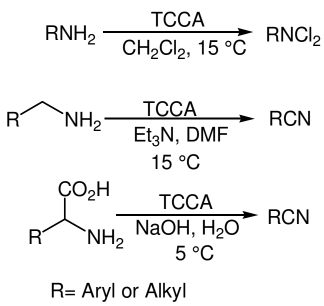
Fluorinated alcohols were also oxidized to aldehydes by the use of TCCA in the presence of TEMPO [30]. TCCA was used for the conversion of primary alcohols and diols to methyl esters and lactones, respectively, by refluxing in dichloromethane (Scheme 17) [31].



Scheme 17

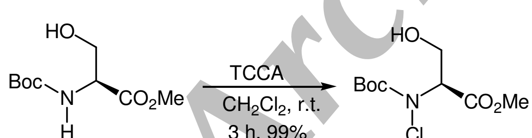
Chlorination Reactions

TCCA was efficiently used for a series of chlorination reactions of different compounds such as amines, amides, alkenes, alkynes, aromatic rings, alcohols, carbonyls and *etc*. The reaction between amines or α-aminoacids with TCCA was studied under various conditions; *N*,*N*-dichloroamines, nitriles and ketones could be obtained from primary amines, while free aminoacids underwent oxidative decarboxylation to the corresponding nitriles of one less carbon atom (Scheme 18) [32].



Scheme 18

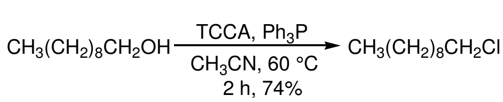
N-Chlorination of various amides, lactams and carbamates were proceeded efficiently by TCCA under very mild condition at room temperature [33]. An interesting example that demonstrates the chemoselectivity of the method is shown in Scheme 19.



Scheme 19

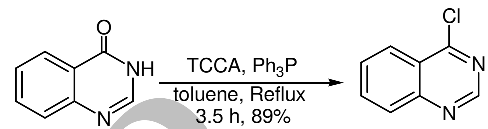
A similar protocol was reported for *N*-chlorination of primary amides in methanol [34].

Hiegel *et al.* reported a procedure for the conversion of alcohols to alkyl chlorides using TCCA in the presence of triphenylphosphine (Scheme 20) [35].



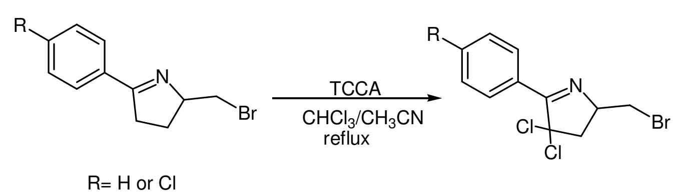
Scheme 20

Chlorination of nitrogen containing π-deficient heteroaromatics was achieved by a similar reagent system in toluene (Scheme 21) [36].



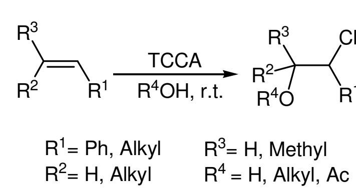
Scheme 21

Regioselective chlorination of isatin at the 5-position and also deactivated aromatic compounds, such as nitrobenzene was carried out by TCCA in H_2SO_4 [37]. An interesting example of application of TCCA as a chlorinating agent was described in the synthesis of some cyclic dichloroimines (Scheme 22) [38].



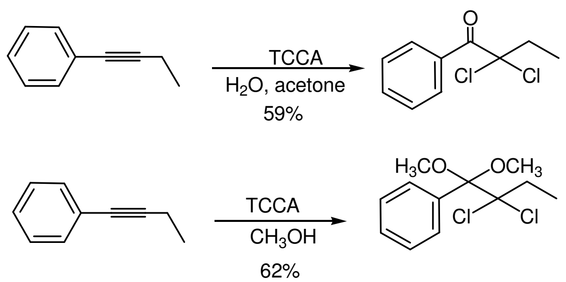
Scheme 22

The preparation of diverse *β*-chloroethers, *β*-chloroacetates and chlorohydrins was achieved by the reaction of alkenes with TCCA in alcohols (MeOH, EtOH, *i*-PrOH and *t*-BuOH), acetic acid or aqueous acetone, respectively (Scheme 23) [39].



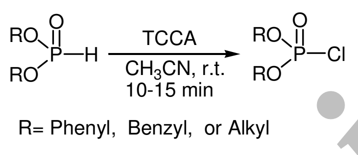
Scheme 23

TCCA was reacted with alkynes in the presence of water in acetone or acetonitrile to form α,α-dichloro ketones and in methanol to form α,α-dichlorodimethyl ketals (Scheme 24) [40].



Scheme 24

Carboxylic acids were chlorinated in the α-position by heating with TCCA after formation of a small amount of the acid chloride using PCl_3 [41]. The synthesis of dialkyl chlorophosphates was described by Acharya *et al.* from the reaction of dialkyl phosphite with TCCA in short reaction times at room temperature (Scheme 25) [42].

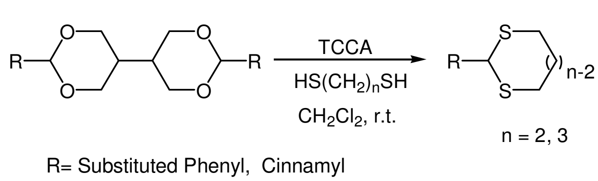


Scheme 25

Treatment of styrene-butadiene rubber with TCCA was reported to chlorinated the rubber and improved its adhesion properties [43,44].

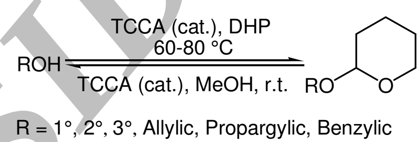
Cleavage and Formation of Carbon-Oxygen and Carbon-Sulfur Bonds

TCCA has efficiently been used for the cleavage and formation of carbon-oxygen and carbon-sulfur bonds. Firouzabadi *et al.* reported the trans thioacetallization of diacetals of 2,2-bis(hydroxymethyl)-1,3-propanediol in dichloromethane at room temperature (Scheme 26) [45].

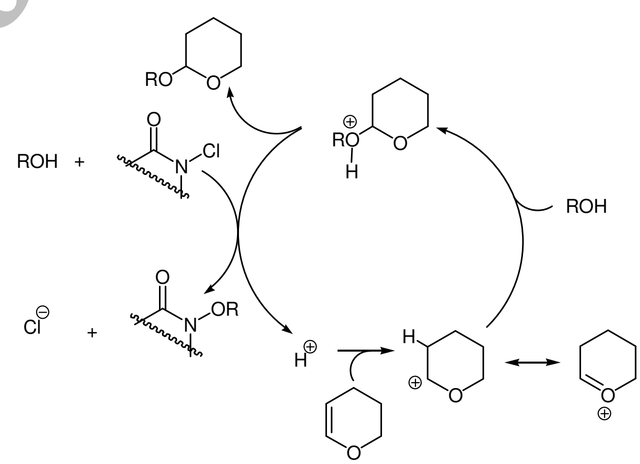


Scheme26

They have also reported an easy and general method for deprotection of thioacetals to their corresponding carbonyl compounds using TCCA/silica gel in the presence of water [45]. Similar reactions were also carried out in non-aqueous conditions ($CHCl_3$ and DMSO) at room temperature [46]. The same group took advantage of TCCA in catalytic preparation and cleavage of THP-ethers of various hydroxy functional groups with high yields (Scheme 27) [47]. A mechanism was proposed for these transformations (Scheme 28).

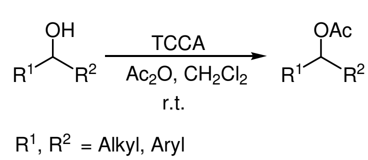


Scheme 27



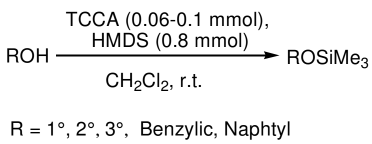
Scheme 28

Acylation of primary, secondary and tertiary alcohols was achieved by the reaction with acetic anhydride and TCCA at room temperature in good to excellent yields (Scheme 29) [48].



Scheme 29

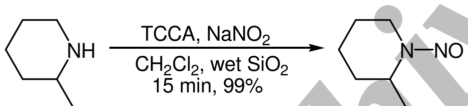
A novel and efficient trimethylsilylation of various alcohols and phenols was efficiently carried out with hexamethyldisilazane (HMDS) in the presence of catalytic amounts of TCCA in good to excellent yields in dichloromethane at room temperature (Scheme 30) [49].



Scheme 30

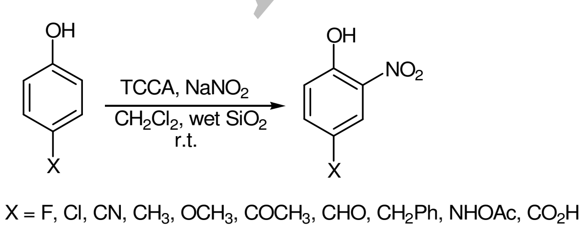
Miscellaneous Reactions

A combination of TCCA and sodium nitrite in the presence of wet SiO_2 has been used for the nitrosation of *N*,*N*-dialkyl amines under mild and heterogeneous conditions [50]. For example 2-methylpiperidine was converted to its *N*-nitroso derivative in short time with quantitative yield (Scheme 31).



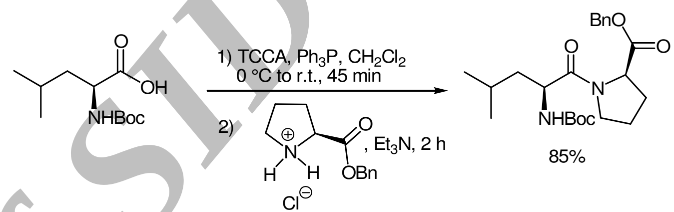
Scheme 31

The same reagent system was used for the mononitration of *p*-substituted phenols at room temperature in good yields (Scheme 32) [51].



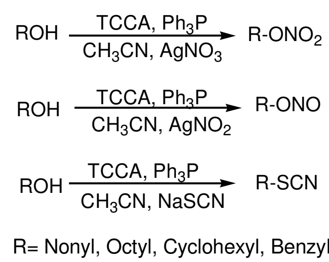
Scheme 32

Dinitrophenols were also obtained in a similar way but under solid-phase reaction conditions [52]. The reaction of TCCA and triphenylphosphine in the presence of carboxylic acids resulted in the *in situ* formation of the corresponding acid chlorides [53]. Subsequent addition of amines or alcohols, in the presence of a tertiary amine, afforded the corresponding amides, or esters, in good to excellent yields. The method was interestingly applied to the synthesis of a protected dipeptide (Scheme 33).



Scheme 33

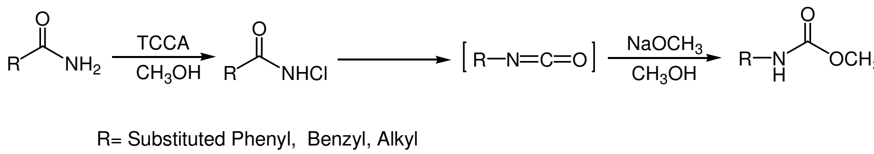
Alcohols were converted into alkyl nitrates, nitrites or thiocyanates by the action of TCCA and triphenylphosphine along with silver nitrate, silver nitrite, or sodium thiocyanate, respectively (Scheme 34) [54].



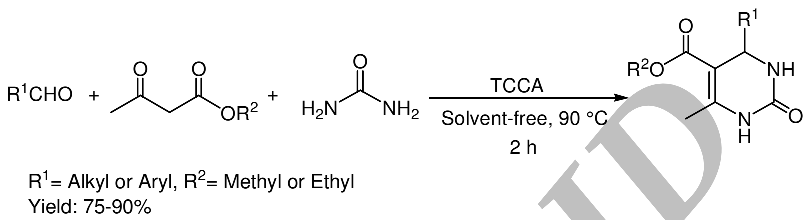
Scheme 34

Amides were chlorinated on nitrogen using TCCA and the produced *N*-chloroamides were then rearranged to the corresponding methyl-*N*-substituted carbamates by sodium methoxide in methanol [55]. Isocyanates were suggested as the intermediates (Scheme 35).

TCCA was used efficiently for the synthesis of 3,4-dihydropyridine-2(1*H*)-ones through the three-component Biginelli reaction of a *β*-ketoester, an aldehyde and urea (Scheme 36) [56]. TCCA has been used as an initator for the



Scheme 35

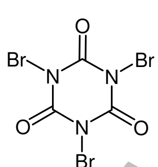


Scheme 36

metal-catalyzed living radical polymerization of methyl methacrylate [57].

TRIBROMOISOCYANURIC ACID AND SODIUM MONOBROMOISOCYANURATE

There are few reports on the application of tribromoisocyanuric acid [58a-d] (TBCA, **3**) and sodium monobromoisocyanurate (SMBI, **4**) in the bromination of aromatic compounds.



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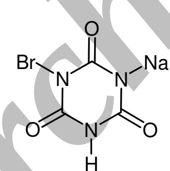
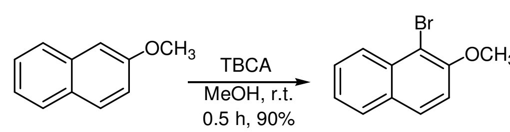


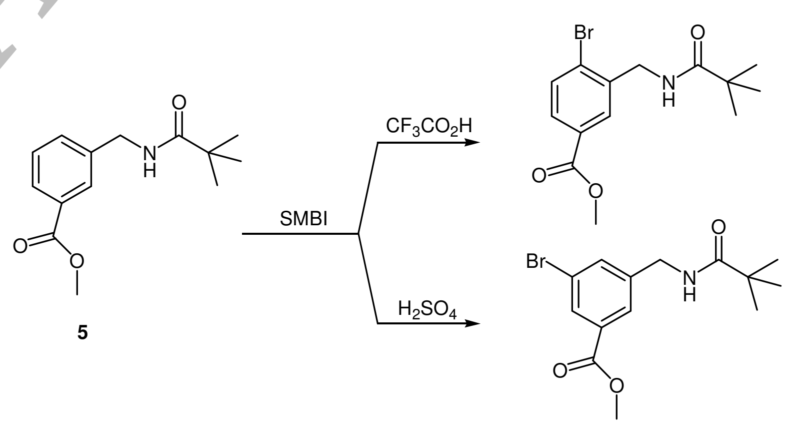
4

An efficient and highly regioselective bromination of activated aromatic rings promoted by TBCA through *in situ* generation of Br^+ has been developed by de Almeida *et al.* [58a]. For example, monobromination of 2-methoxy-naphtalene was carried out in excellent yield after a short reaction time (Scheme 37). Also, Niknam *et al.* have reported



Scheme 37

nitration of phenols, silylation of alcohols and oxidation

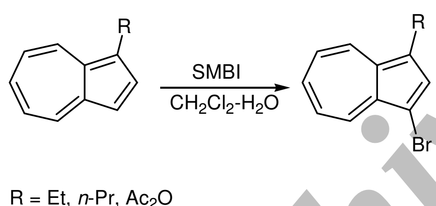


Scheme 38

of urazoles using TBCA [58b-d].

A variety of aromatic compounds with both activating and deactivating substituents were brominated with SMBI [59]. Diethyl ether, diethyl ether-methanesulfonic acid, trifluoroacetic acid or sulfuric acid was employed as solvents. Thus, nitrobenzene were conveniently brominated in sulfuric acid, benzene was readily monobrominated in diethyl ether-methanesulfonic acid and phenol was selectively brominated at the *ortho* position under milder conditions in refluxing diethyl ether. An interesting example was selective bromination of compound **5** by changing the solvent (Scheme 38).

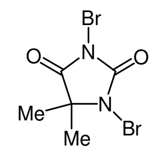
Bromination of some azulene derivatives were achieved by SMBI. Bromination in dichloromethane gave the products in low yields, while the reactions in dichloromethane-water gave good yields of the desired compounds (Scheme 39) [60]. The following mechanism was suggested for these reactions (Scheme 40).



Scheme 39

1,3-DIBROMO-5,5-DIMETHYLHYDANTOIN

1,3-Dibromo-5,5-dimethylhydantoin (DBH, **6**) with the commonly used trade name Brom-55, is a cream to pale-brown powder which melts at 186-192 ºC. This reagent is sparingly soluble in carbon tetrachloride, benzene and water (0.06%, 1.1%, and 0.1% at 20 ºC, respectively). Due to its economic advantages, DBH has found widespread applications in industrial processes such as swimming-pool sanitizer, brominating agent for ethylene propylene diene monomer rubber (EPDM) to improve ozone resistance, additive in plastics to promote photodegradation and as a fungicide to preserve fresh fruits [61-68].



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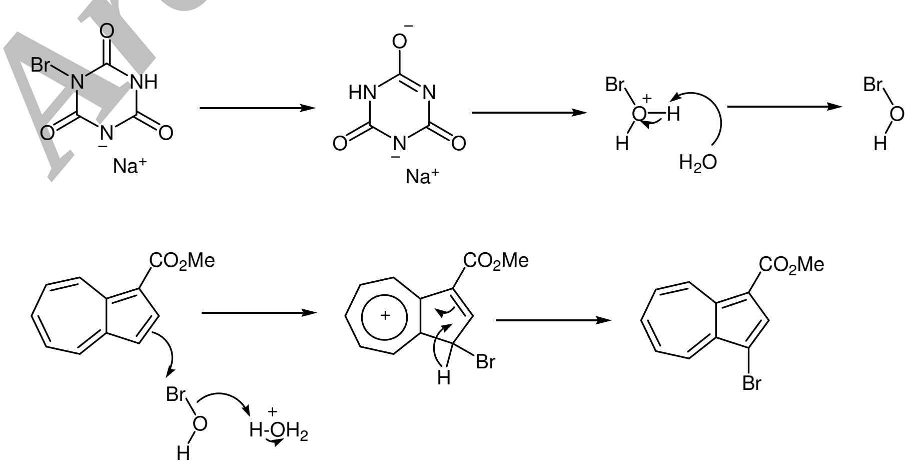
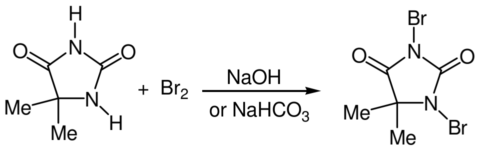
Among the methods, which were reported for the preparation of DBH [69-72], the bromination of 5,5-dimethylhydantoin (DMH) in the presence of NaOH or



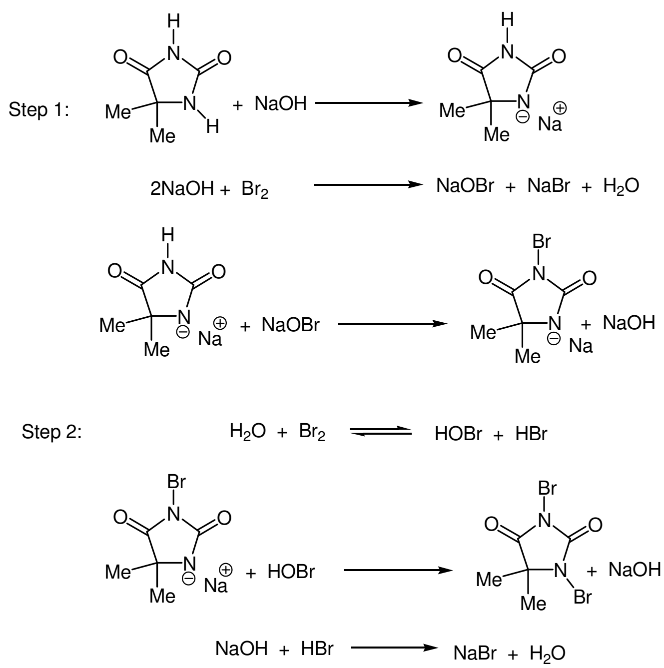
Scheme 40

$NaHCO_3$ was studied with precision (Scheme 41) [73]. It was



Scheme 41

reported that the mechanism of the reaction consists of two bromination steps (Scheme 42).

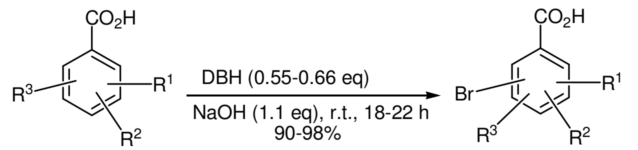


Scheme 42

The application of DBH in organic reactions mainly can be studied in the following sections.

Halogenation Reactions

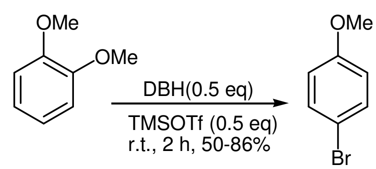
Bromination reactions. In 1993, Auerbach and co-workers reported that DBH in aqueous NaOH can be used as an efficient reagent for the bromination of activated benzoic acids [74]. They also showed that DBH gave better yields than NBS (Scheme 43).



Substrate	Product
R^1, R^2, R^3 = 3,4,5-(OMe)$_3$	R^1, R^2, R^3 = 3,4,5-(OMe)$_3$, 2-Br
R^1, R^2 = H; R^3 = 2-OMe	R^1, R^2 = H; R^3 = 2-OMe, 5-Br
R^1 = H; R^2, R^3 = 2,3-(OMe)$_2$	R^1 = H; R^2, R^3 = 2,3-(OMe)$_2$, 6-Br

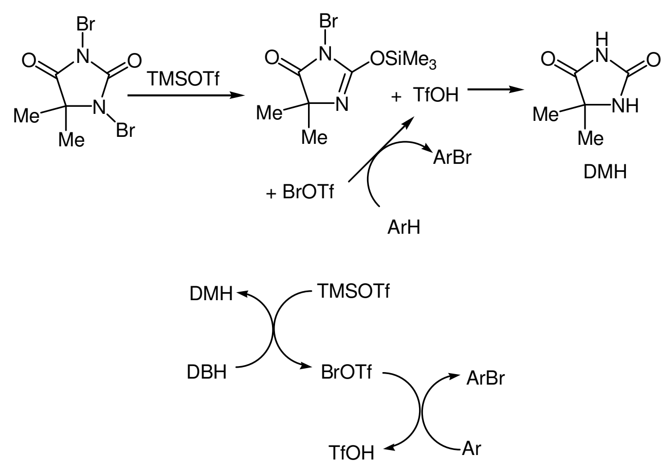
Scheme 43

Studies cleared that the rate of the bromination of various aromatic derivatives substituted with electron donating groups, with DBH, considerably enhanced in the presence of trimethylsilyltrifluoromethanesulfonate (TMSOTf) [75] (Scheme 44).



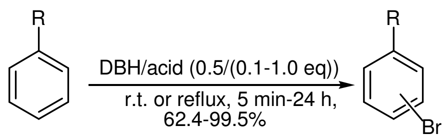
Scheme 44

The authors explained activation of DBH in the presence of TMSOTf *via* bromination of triflate, as a reactive intermediate (Scheme 45).



Scheme 45

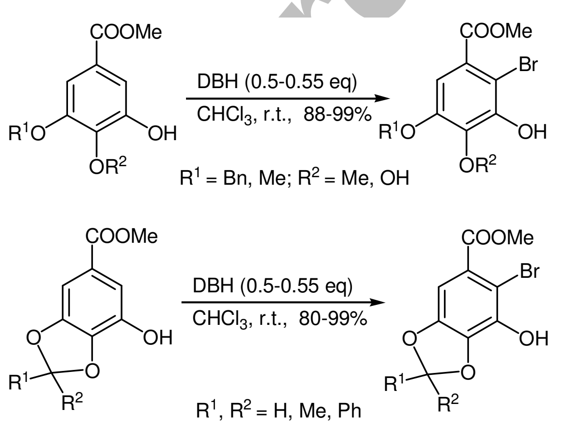
Similarly, Eguchi and co-workers used DBH in the presence of organic and inorganic acids with *pKa* values less than -2 to get the monobromide in excellent yields [76]. Very good yields were obtained even for aromatics having electron-withdrawing substituents. In some cases, catalytic amounts of acids were sufficient (Scheme 46).



R	H_2SO_4	CF_3SO_3H
NO_2	75%	87%
CF_3	81%	86%
OMe	97%	97%
CO_2Me	71%	76%

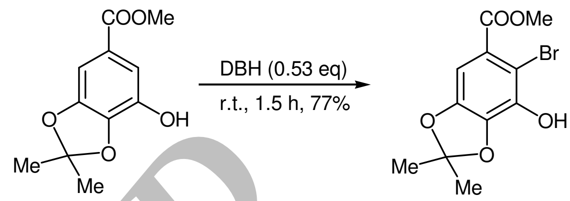
Scheme 46

In 2005, Tsuboi and co-workers have found that DBH (0.5-0.55 eq.) is able to act as an efficient reagent for conversion of phenols and polyphenols to their corresponding *ortho*-monobromides in good to excellent yields (Scheme 47) [77].



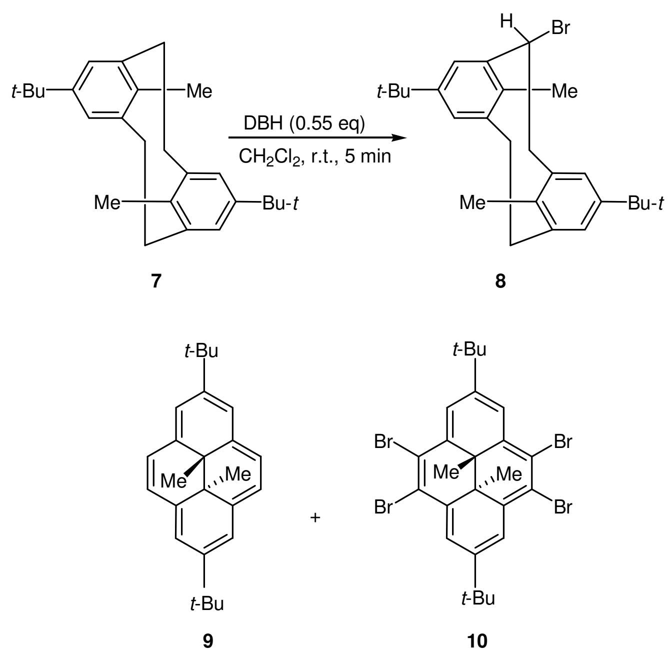
Scheme 47

They also studied the regioselective bromination of pyrogallol derivatives by DBH, which gave single monobromides in 1.5 h at room temperature (Scheme 48) [78].



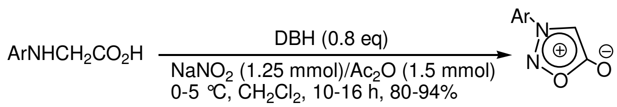
Scheme 48

Treatment of 5,13-di-*tert*-butyl-8,16-dimethyl [2.2] metacyclophane **7** with DBH (0.55 eq.) in CH_2Cl_2 at room temperature led to the introduction of bromine on the bridged methylene group for the first time (Scheme 49) [79]. The reaction was accompanied by the formation of two by products **9** and **10**. The yields of **9** and **10** depended on the amounts of DBH, so in the presence of 3.1 eq. of DBH only compound **10** was obtained in 98% yield.



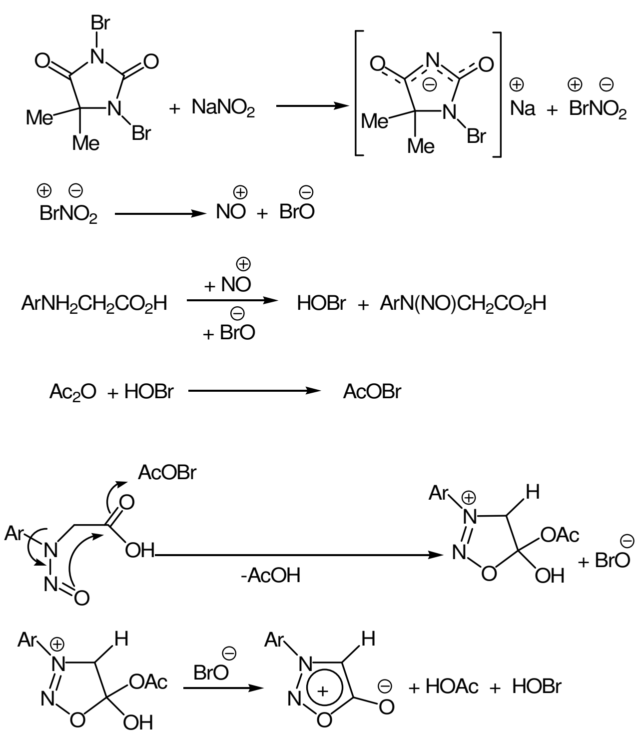
Scheme 49

In 2006, Azarifar *et al*. reported an efficient method for the conversion of various *N*-arylglycines to sydnones using DBH in the presence of $NaNO_2/Ac_2O$ under mild and neutral conditions (Scheme 50) [80]. The following mechanism was



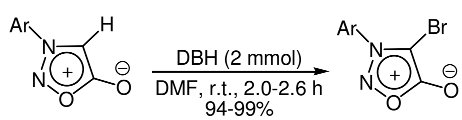
Scheme 50

proposed for these transformations (Scheme 51).



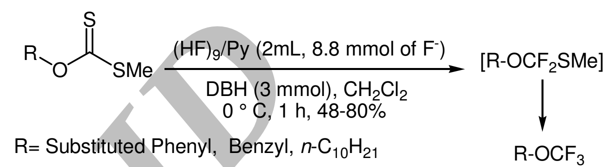
Scheme 51

They also showed that DBH is able to promote the bromination of sydnones to their 4-bromo-substituted congeners in excellent yields in DMF at room temperature (Scheme 52).



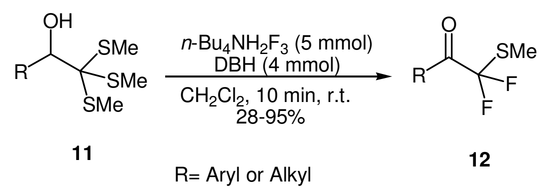
Scheme 52

Flourination reactions. Hiyana *et al.* reported the oxidative desulfurization-fluorination of methyl xanthates with $(HF)_9$/pyridine and DBH (Scheme 53) [81]. Under the reaction conditions, trifluoromethyl ethers (R-OCF_3) were produced through R-OCF_2SMe intermediates.



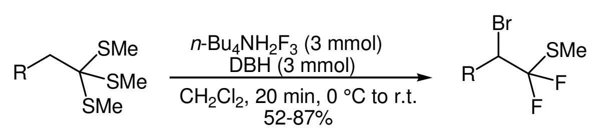
Scheme 53

They also showed that β-hydroxy orthothioesters **11** derived from both aromatic and aliphatic aldehydes were successfully converted into their corresponding difluoro(methyl thio)methyl ketones **12** using n-$Bu_4NH_2F_3$ and DBH. Reactions were performed in CH_2Cl_2 at room temperature (Scheme 54) [82].



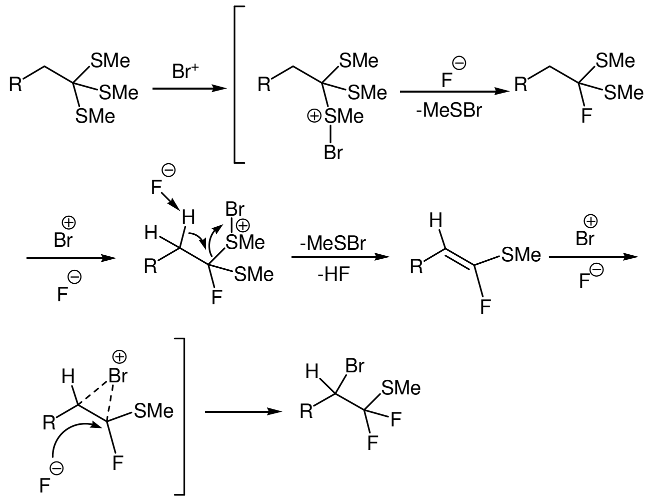
Scheme 54

Correspondingly, when orthothioesters were selected as the substrate the monobromo- difluorinated compounds were obtained as the main products (Scheme 55) [83]. A



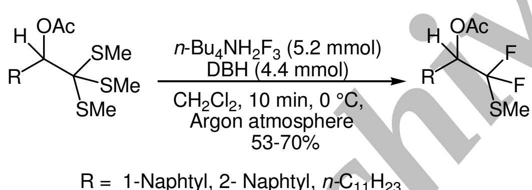
Scheme 55

mechanism which initiated by the electrophilic attack of Br^+ at the sulfur atom of the substrate has been suggested (Scheme 56).



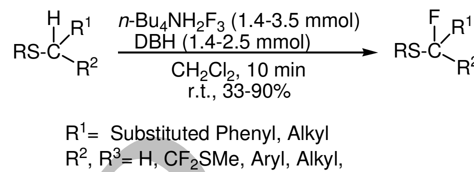
Scheme 56

They also found that when RCH(OAc)C(SMe)$_3$ was used instead of RCH$_2$C(SMe)$_3$, the corresponding difluoro acetate was obtained as the main product (Scheme 57) .



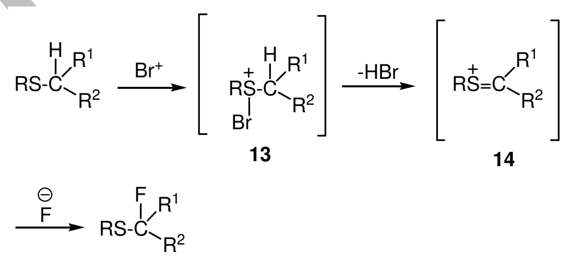
Scheme 57

Furuta *et al.* reported that various organic sulfides, on treatment with n-Bu$_4$NH$_2$F$_3$/DBH, were efficiently converted to α-fluorosulfides (Scheme 58) [84,85]. The formation of the



Scheme 58

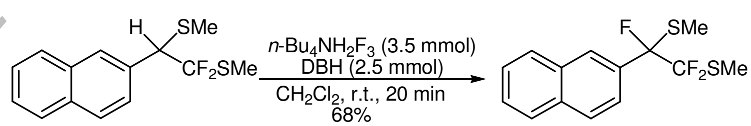
product can be rationalized by the following mechanism (Scheme 59). On the basis of the proposed mechanism, electrophilic attack of Br$^+$ to organic sulfide produces a sulfonium ion **14**, which is attacked by the fluoride ion to give the final product. The reaction of RCH(SMe)CF$_2$SMe, under



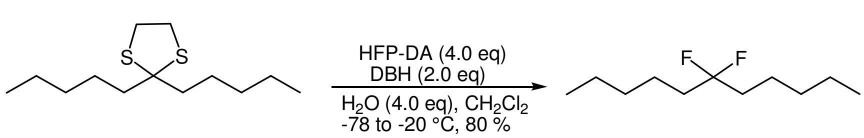
Scheme 59

the same conditions, ended up with the formation of trifluorosulfides, [RCF(SMe)CF$_2$SMe], as the main products (Scheme 60).

Shimizu *et al.* reported an efficient method for the



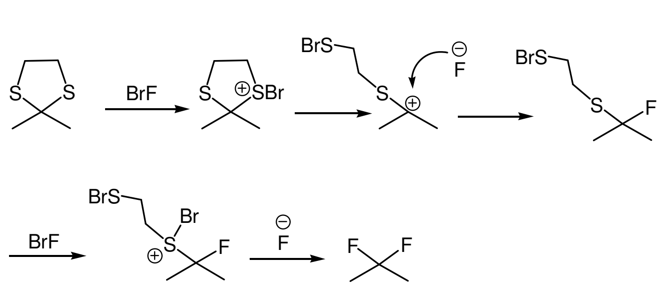
Scheme 60



Scheme 61

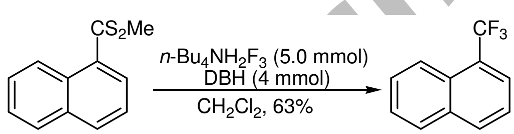
conversion of gem-disulfides to the corresponding gem-difluorinated compounds by a combination of hexafluoropropene-dimethylamine and DBH (Scheme 61) [86].

Using this method, 1,3-dithiolanes derived from ketones gave better results than those from aldehydes. The probable mechanism of the reaction is shown in Scheme 62.



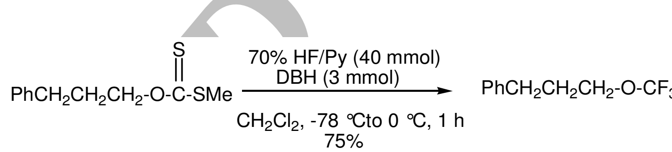
Scheme 62

Furuta *et al.* have found that when methyl arenecarbodithioates and α,β-unsaturated carbodithioates were treated with n-$Bu_4NH_2F_3$ in the presence of DBH, trifluoromethyl and 3,3,3-trifluoropropenyl substituted aromatic compounds were obtained in acceptable yields (Schemes 63 and 64) [87].

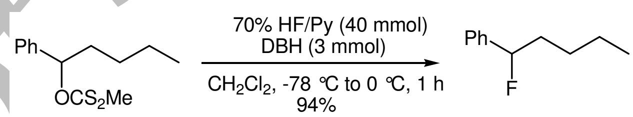


Scheme 63

They have also reported a mild method for the preparation of trifluoromethyl ethers (R-OCF_3). The reaction was carried out by the reaction of dithiocarbonates (R-OCS_2Me) with a reagent system consisting of 70% HF/Pyridine and DBH (Scheme 65) [88]. When the reaction was applied to $ROCS_2$Me wherein R = secondary alkyl, tertiary alkyl or benzylic group, fluorination was leading to corresponding alkyl fluorides (R-F) (Scheme 66).

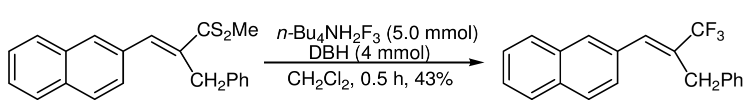


Scheme 65

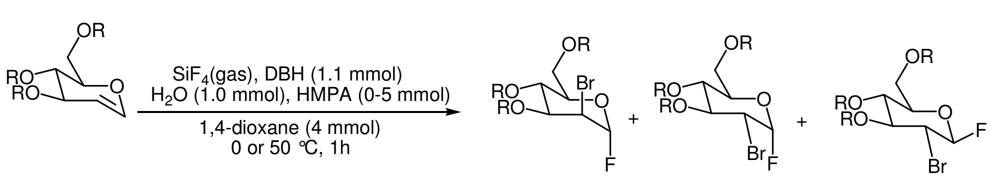


Scheme 66

Due to their stability and stereoselectivity on the glycoside synthesis, the glycosyl fluorides have recently received considerable attention [89]. Among different methods reported for the preparation of glycosyl fluorides, bromofluorination of glycals with SiF_4/DBH/H_2O reagent system in 1,4-dioxane in the presence of HMPA was considered as one of the most useful and stereoselective methods for the preparation of bromofluoro sugars [90] (Scheme 67). Stereoselectivity of the reaction is strongly influenced by the solvent polarity. In the



Scheme 64

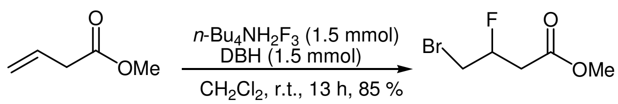


R= Benzyl and Acetyl

Scheme 67

absence of HMPA, formation of the α-fluorides predominated with ratio of 74:26, and the addition of HMPA improved the selectivity in favor of the α-isomers. The best stereoselectivity was obtained when the reaction was carried out in the presence of 3.0 eq. of HMPA, in which the α- *vs.* *β*-isomer ratio was 92:8.

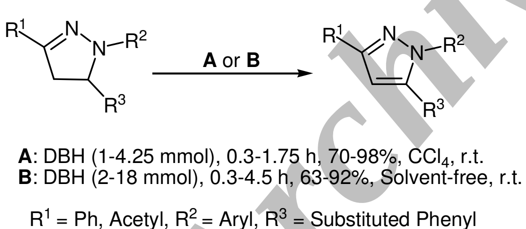
Hiyama *et al.* has also reported that when alkene was treated with $KHF_2/HF/n\text{-}Bu_4NF/DBH$ reagent system, the related bromofluorinated product was obtained in good to high yields (Scheme 68) [91]. The stereochemistry of the addition of F and Br was anti for all of the olefins.



Scheme 68

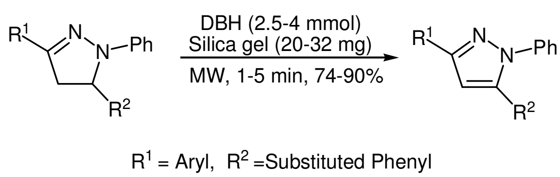
Oxidation Reactions

In 2004, oxidation of 1,3,5-trisubstituted pyrazolines to the corresponding pyrazoles using DBH under both heterogeneous and solvent-free conditions was reported by Azarifar *et al.* (Scheme 69) [92].



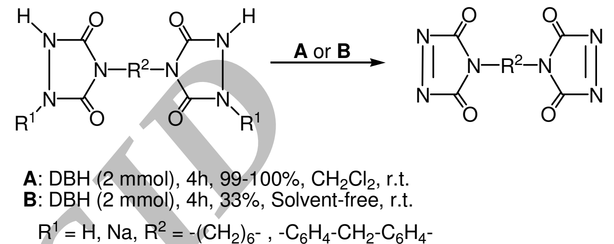
Scheme 69

The same group has also shown that when the reaction was carried out in the presence of silica gel under microwave irradiation, the products were obtained during very short reaction times (Scheme 70) [93].



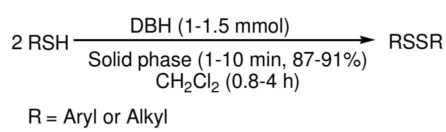
Scheme 70

DBH has also been used for the efficient oxidation of mono and bis-urazoles to their corresponding triazolinediones both in solution and under solvent-free conditions (Scheme 71) [94].



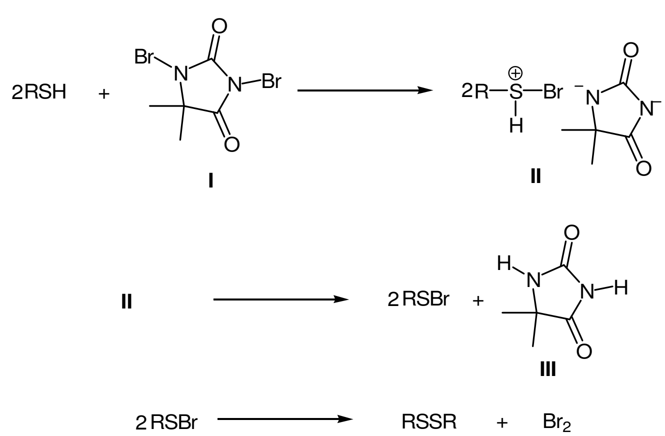
Scheme 71

Khazaei *et al.* reported a simple method for the oxidation of thiols to disulfides by the use of DBH in dichloromethane (Scheme 72) [95]. An inconceivable decrease in the reaction time was observed in the absence of solvent.



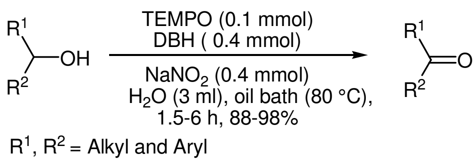
Scheme 72

A mechanism was proposed for this reaction (Scheme 73).



Scheme 73

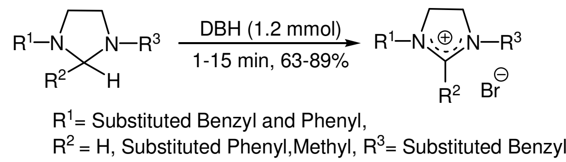
The same subject has also been investigated by another group in 2005 [96]. DBH in accompanying with $NaNO_2$ was used as a co-catalyst for the acceleration of the aerobic oxidation of benzylic alcohols in water catalyzed by TEMPO (Scheme 74) [97]. All reactions were performed at 80 ºC and the products were obtained in good to high yields.



Scheme 74

Recently, Rievera *et al.* reported a suitable method for the synthesis of 5-substituted-2-amino-1,3,4-oxadiazoles, as biologically active important molecules, *via* oxidative cyclization of thiosemicarbazides using DBH in the presence of potassium iodide (Scheme 75) [98]. The main advantage of this method is its applicability for the large scale synthesis of the hydroxyl oxadiazoles.

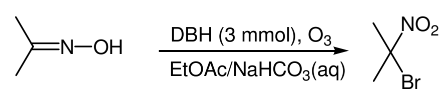
In 2006, Salerno *et al.* have used DBH as an efficient dehydrogenating agent for the oxidation of *N*,*N*´-dibenzyl- and *N*-aryl-*N*´-benzyl-imidazolidines to their 4,5-dihydro-1*H*-imidazolium salts (Scheme 76) [99]. The main advantages of the selected method are: low reaction times, obtaining relatively pure products and high yields. Since the rate of the reaction did not change in the presence of a radical initiator (benzoyl peroxide) or a radical inhibitor (butylated hydroxy toluene, BHT), an ionic mechanism, which involved bromination of imidazolidine`s nitrogen, followed by deprotonation and displacement of a bromide ion, was proposed for the reaction (Scheme 77).



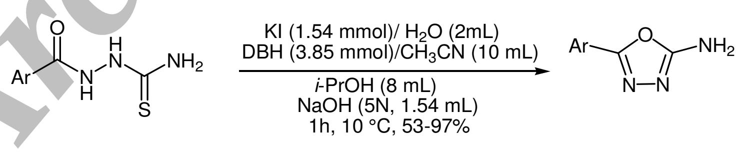
Scheme 76

Miscellaneous Reactions

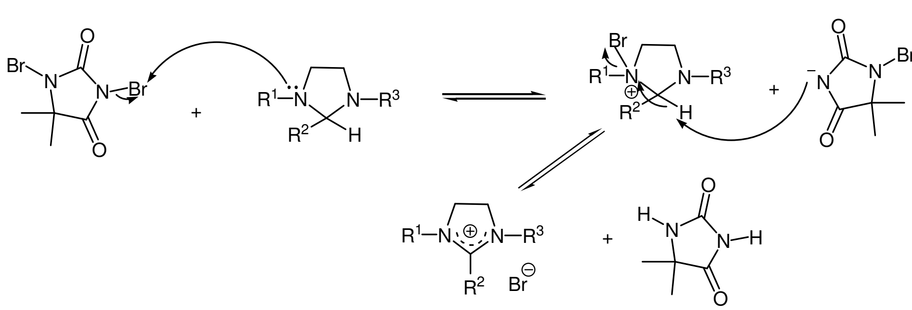
Walters *et al.* studied the use of DBH for the oxidation of hydroxylamines to gem-halonitro compounds in the presence of ozone (Scheme 78) [100]. The bromo derivatives were obtained in 44-73% yields.



Scheme 78



Scheme 75

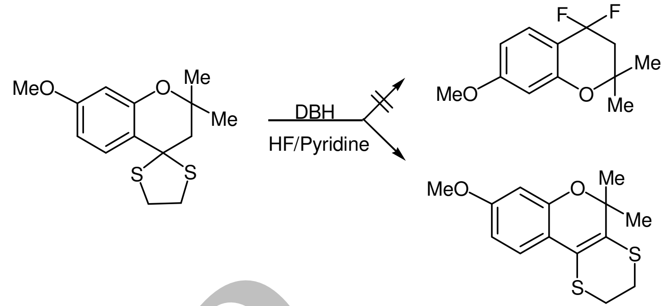


Scheme 77

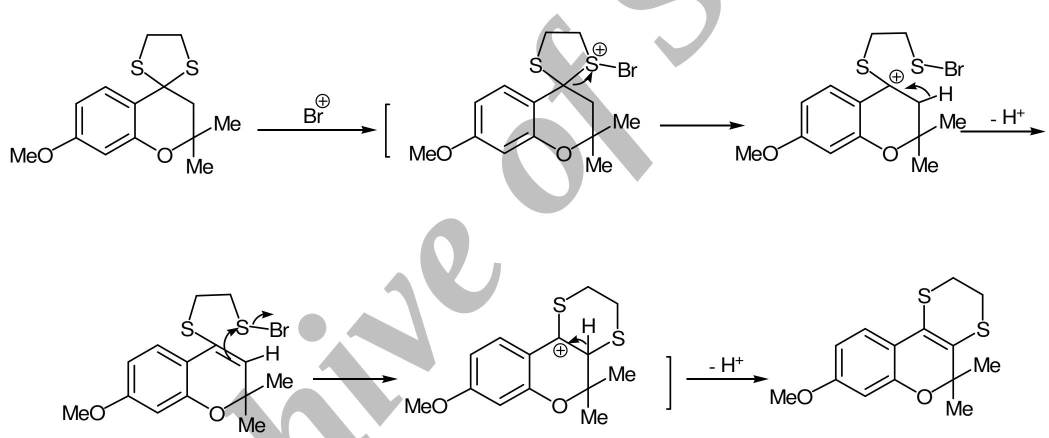
When 1,3-dithiolanes bearing a phenyl or substituted aromatic group and a methyl (or methylene) group attached to C-2 were treated with DBH in the presence of HF/pyridine, a rearrangement took place instead of gem-difluorination (Scheme 79) [101]. A mechanism was proposed for this rearrangement, which is shown in Scheme 80.

DBH was also applied for the synthesis of diglicodeoxynucleotides containing 2′-*O*-(trifluoromethyl) adenosine in the presence of HF/pyridine (Scheme 81) [102]. Using this method, products were obtained in relatively acceptable yields under mild reaction conditions.

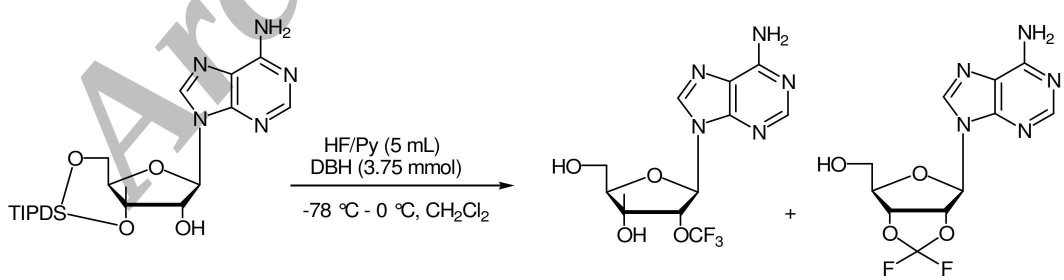
Madhusudan *et al.* reported the facile conversion of glycosyl *S,S*-acetals to their corresponding *O,O*-acetals using DBH under mild and neutral conditions (Scheme 82) [103].



Scheme 79

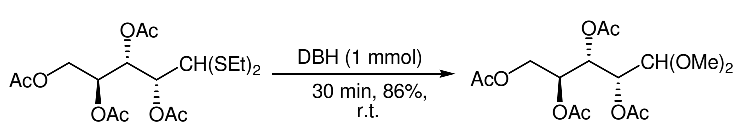


Scheme 80



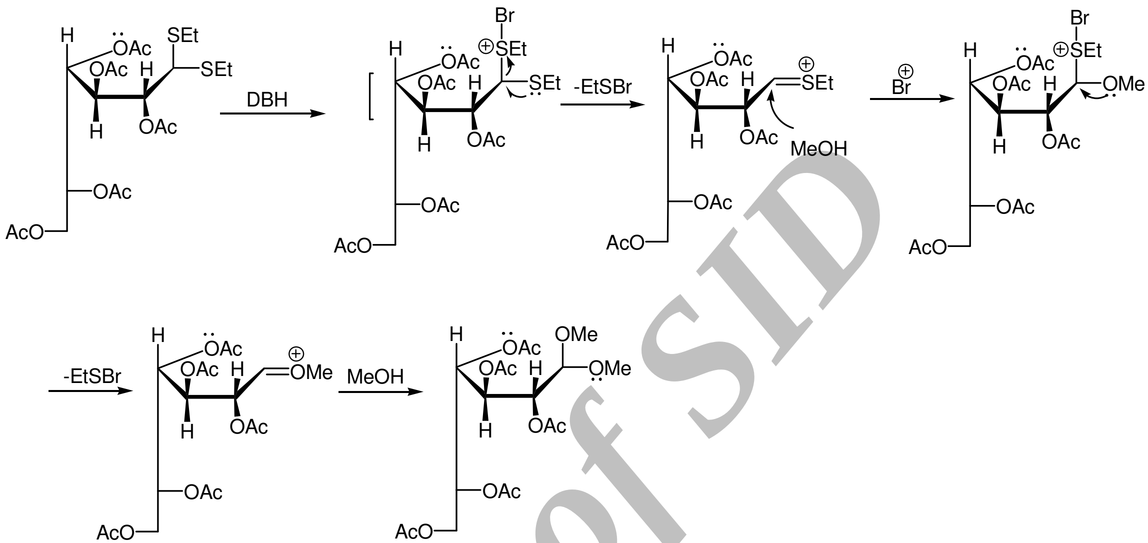
TIPDS = tetraisopropyldisiloxane-1,3-diyl

Scheme 81

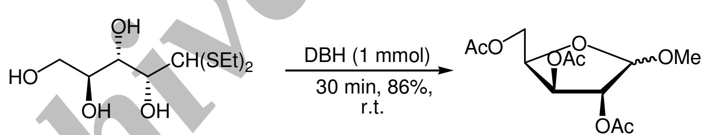


Scheme 82

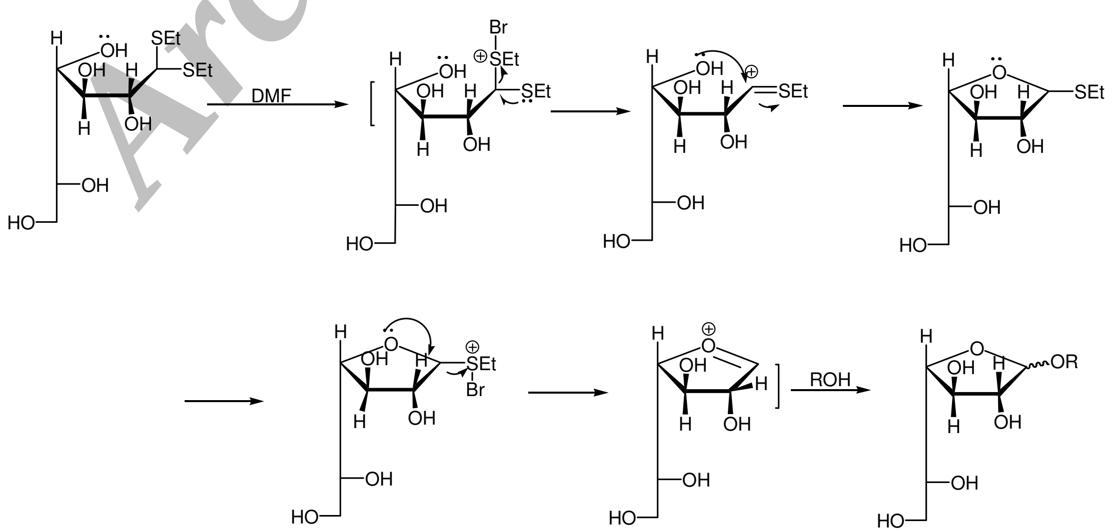
The proposed mechanism of this reaction is illustrated in (Scheme 83). When glyclic glycosyl *S,S*-acetals were reacted under the same conditions, glycofuranosides were obtained in good to high yields (Scheme 84). In the case of



Scheme 83



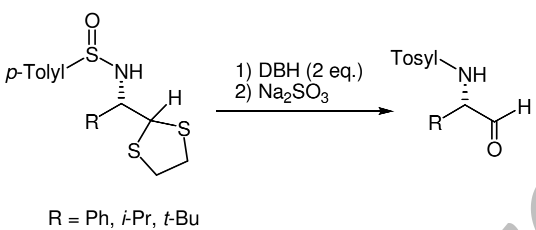
Scheme 84



Scheme 85

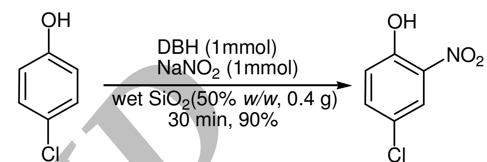
glycofuranoside formation, the authors proposed that product was formed by intramolecular nucleophilic attack from the hydroxyl group at C-4 following by a nuclophilic attack of the alcohol at C-1 (Scheme 85).

Because of the unstability of α-aminoaldehydes, which are reckoned as extremely valuable chiral building blocks in asymmetric synthesis [104], the preparation of *N*-protected derivatives of these compounds is attracted the attention of many organic chemists. Davis *et al.* reported that the hydrolysis of sulfimine derived *N*-sulfinyl-α-amino-1,3-dithianes with aqueous DBH affords the corresponding *N*-tosyl-α-aminoaldehydes in good yields and high enantiomeric purities (Scheme 86) [105].



Scheme 86

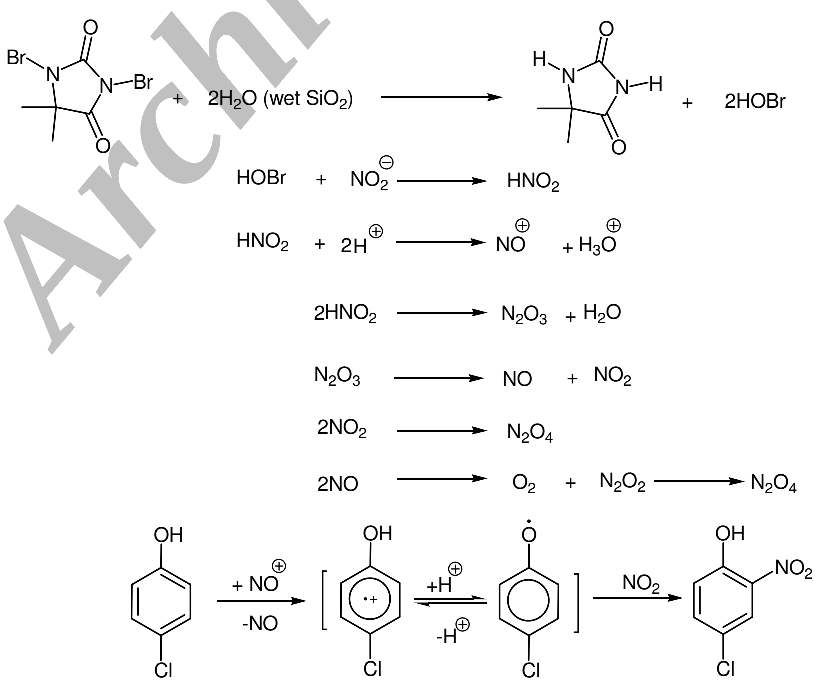
Recently, DBH/$NaNO_2$/wet SiO_2 has been used as an efficient reagent system for the direct nitration of phenols (Scheme 87) [106]. All reactions were performed at room temperature and under completely heterogeneous conditions.



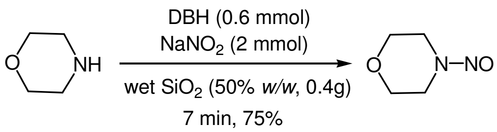
Scheme 87

The reaction did not proceed in the absence of wet SiO_2. The following mechanism was proposed for the description of the reaction pathway (Scheme 88).

In the same manner, when *N*,*N*-dialkylamines were treated with DBH/$NaNO_2$/wet SiO_2 reagent system, their corresponding *N*-nitrosated derivatives were obtained in good to excellent yields (Scheme 89) [107]. The reaction conditions are very mild and completely heterogeneous.

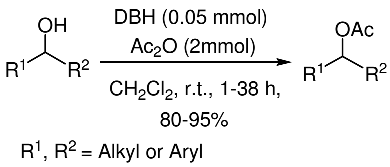


Scheme 88



Scheme 89

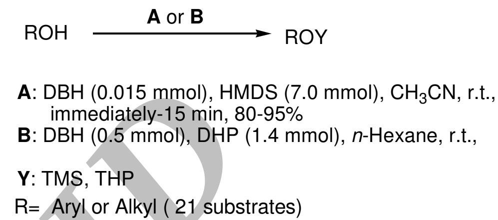
Recently, an efficient and high yielding method for the acylation of alcohols with acetic anhydride using DBH has been reported (Scheme 90) [108]. The proposed mechanism,



Scheme 90

which was based on activation of Ac_2O by the *in situ* generated H^+, is shown in Scheme 91.

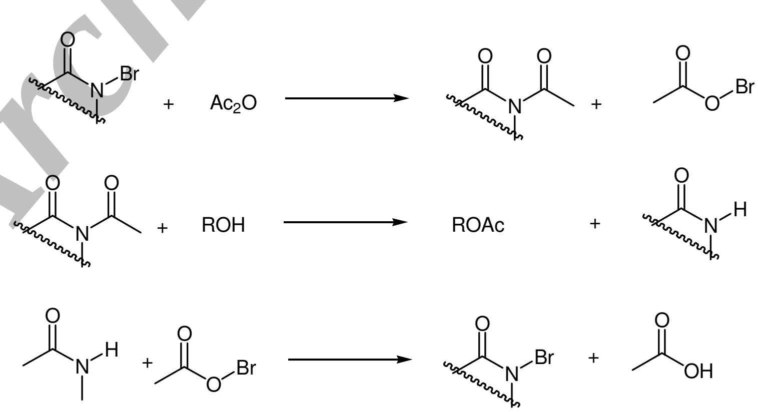
DBH efficiently enhanced the rate of trimethylsilylation of different types of alcohols with HMDS [109]. Alcohols were also converted to their corresponding tetrahydropyranyl ethers with 3,4-dihydro-2*H*-pyran in the presence of DBH. The method is mild and the products were obtained in high yields (Scheme 92). The method was also used for the



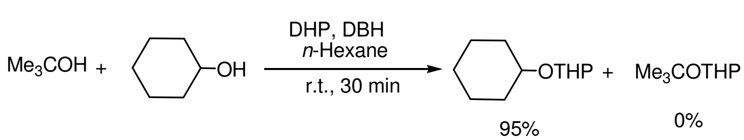
Scheme 92

selective trimethylsilylation or tetra-hydropyranylation of various types of alcohols in the presence of tertiary alcohols (Scheme 93). The mechanism which has been reported for the above mentioned method is the same as that reported for the tetrahydropyranylation of alcohols in the presence of TCCA (Scheme 28).

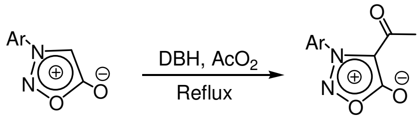
DBH has been found to efficiently catalyze the conversion of various 3-arylsydnones to their corresponding 4-acetyl derivatives in the presence of acetic anhydride under neutral conditions in satisfactory yields (Scheme 94) [110].



Scheme 91



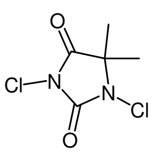
Scheme 93



Scheme 94

1,3-DICHLORO-5,5-DIMETHYLHYDANTOIN

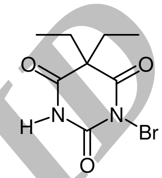
Contrary to DBH, its chlorinated analogue, 1,3-dichloro-5,5-dimethylhydantoin (DCH, **15**), has found very limited applications and only few reports are available on its uses in organic synthesis. These reports are included α-chlorination of acetophenones (Scheme 95) [111], oxidative cleavage of oximes [112,113] and oxidation of urazoles [114].



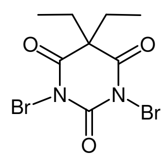
15

1-BROMO-5,5-DIETHYLBARBITURIC ACID AND 1,3-DIBROMO-5,5-DIETHYLBARBITURIC ACID

1-Bromo-5,5-diethylbarbituric acid **16** and its 1,3-dibromo analogue **17** were prepared in 1991 but found little attention of organic chemsits [115]. They have been used for the oxidative

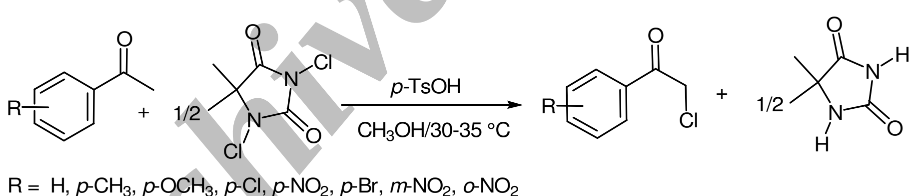


16

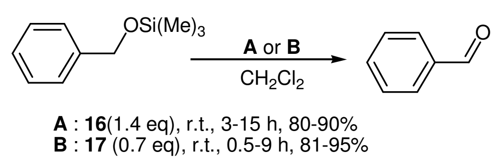


17

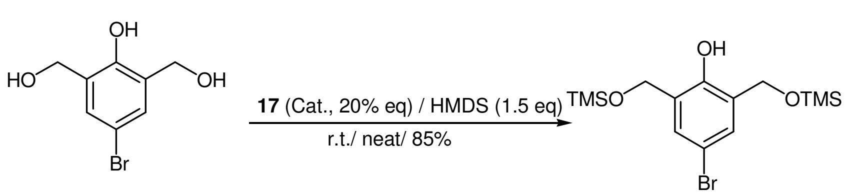
cleavage of different kinds of trimethylsilyl ethers in good yields at room temperature (Scheme 96) [116]. The conversion of benzyl trimethylsilyl ether to benzaldehyde in the presence of both **16** and **17** was conducted in different solvents. The results showed that the efficiency and the yield of the reaction



Scheme 95



Scheme 96



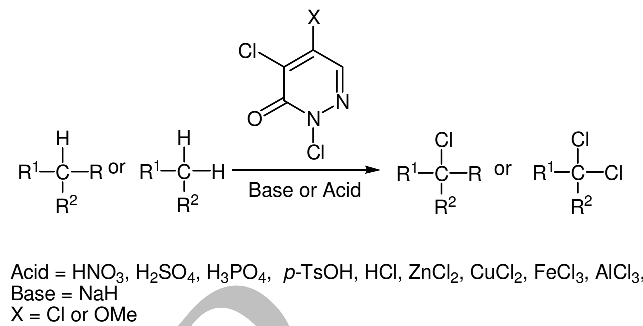
Scheme 97

in dichloromethane was better than in other solvents. THP-ethers remained intact under the reaction conditions.

Silylation of alcohols and polyols is one of the most commonly used methods for their protection. Trimethylsilylation is a classic way to produce volatile derivatives of alcohols and polyols. The application of 17 as a catalyst was described in the protection of different alcohols by HMDS in good to high yields in the absence of solvent at room temperature. A good selectivity was observed for the protection of alcohols over phenols (Scheme 97) [117].

2,4,5-TRICHLORO- AND 2,4-DICHLORO-5-METHOXYPYRIDAZIN-3(2*H*)-ONE

2,4,5-Trichloro- and 2,4-dichloro-5-methoxypyridazin-3(2*H*)-one were synthesised by Park *et al.* as two novel reagents in 2005 [118]. α-Chlorination of active methylene/methine compounds with these reagents in the presence of either Lewis or protic acids in dichloromethane (for Lewis acid) or water (for protic acid) at room temperature gave also α-monochlorides and/or α,α-dichlorides selectively in good to excellent yields (Scheme 98).



Scheme 98

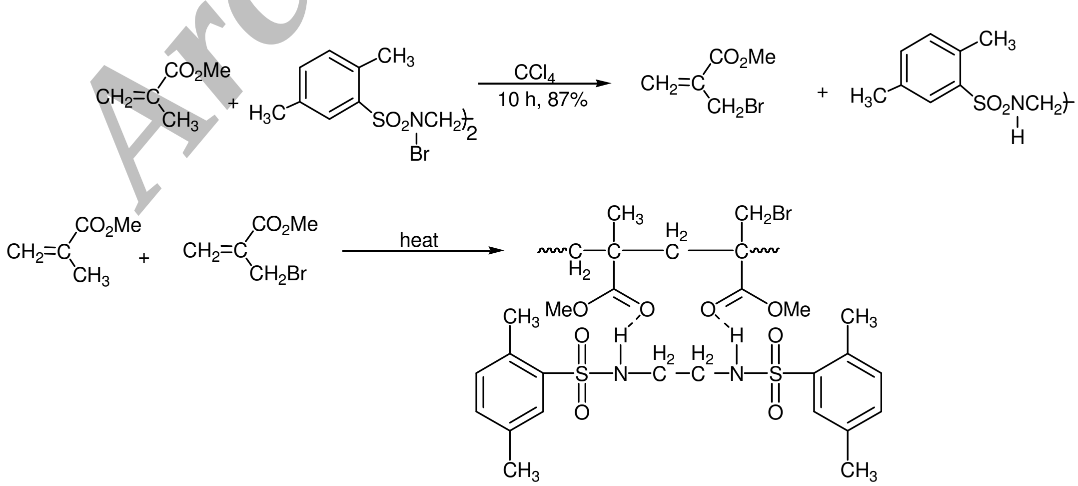
N-HALO SULFONAMIDES

N-halo sulfonamides have been widely used in organic synthesis. They can be applied as halogenating agent or as catalyst in organic transformations. The application of some *N*-halo sulfonamides such as *N,N*-dihalo sulfonamides was reviewed by Koval [119,120]. Herein, application of a broad range of *N*-halo sulfonamides is reviewed.

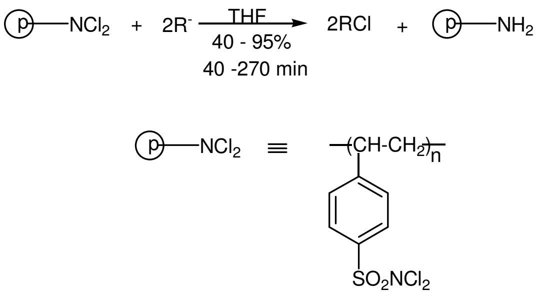
Halogenation Reactions

Khazaei *et al.* have reported a novel compound that was synthesized *via* bromination of methyl methacrylate with high yield. This brominated compound is suitable for polymerization as an adhesive (Scheme 99) [121].

Carbanionic substrates were subjected to chlorination with poly[4-vinyl-*N*,*N*-dichlorobenzenesulfonamide]. Chlorinated products were obtained in good yield and short reaction time under mild condition (Scheme 100) [122].



Scheme 99

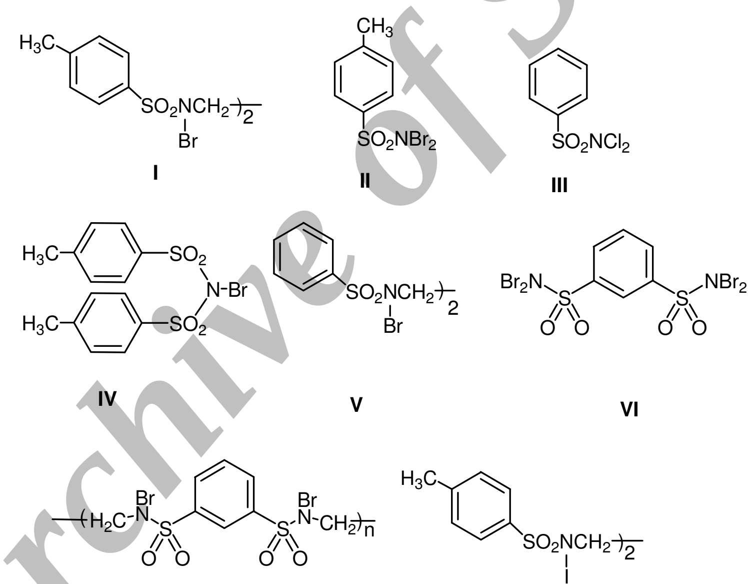


Scheme 100

Recently some new *N*-halo sulfonamides have been reported as chemoselective brominating agents for a broad range of organic compounds (Scheme 101) [123-132]. Bromination of allylic compounds was described by using *N,N′*-dibromo-*N,N′*-ethanediylbis(2,5-dimethylbenzene)sulfonamide (Scheme 102) [134].

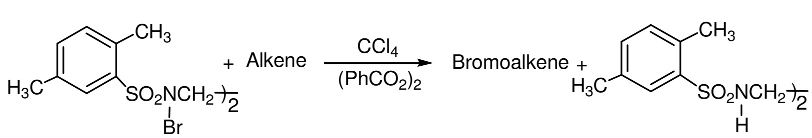
Regioselective bromination of activated aromatic compounds was carried out with *N,N′*-dibromo-*N,N′*-ethanediyl bis(*p*-toluenesulfonamide) (BNBTS) [128].

Ghorbani and Jalili reported the preparation of *N,N′*-tetrabromobenzene-1,3-disulfonamide (TBBDA) and poly *N*-bromobenzene-1,3-sulfonamide (PBBS). These new reagents have been used for bromination of activated aromatic compounds in good yields (Scheme 103) [129].

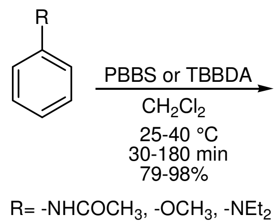


I : *N,N′*-dibromo-*N,N′*-ethanediylbis (*p*-toluenesulfonamide) [BNBTS]
II : *N,N*-dibromo(*p*-toluenesulfonamide)
III :*N,N*-dibromobenzenesulfonamide
IV :*N*-bromobis(*p*-toluenesulfonyl)amine [NBBTA]
V : *N,N′*-dibromo-*N,N′*-ethanediylbisbenzenesulfonamide
VI : *N,N′*-tetrabromobenzene-1,3-disulfonamide [TBBDA]
VII :poly *N*-bromo benzene-1,3-sulfonamide [PBBS]
VIII: *N,N′*-diiodo-*N,N′*-ethanediylbis(*p*-toluenesulfonamide) [NIBTS]

Scheme 101

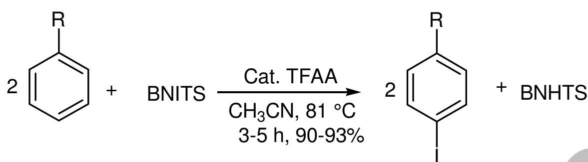


Scheme 102



Scheme 103

N,N′-Diiodo-*N,N′*-ethanediylbis(*p*-toluenesulfonamide) (BNITS) as a novel iodinating agent has been used for iodination of some aromatic compounds in high yields (Scheme 104) [132].



Scheme 104

Cleavage and Formation of Carbon-Hetroatom Bonds

The protection of carbonyl compounds is very important in multistep synthesis. Protected carbonyl compounds such as oximes, semicarbazones, phenylhydrazone derivatives, diacetals, dithianes and *etc*. are easily prepared and are highly stable compounds used extensively for protection, purification and characterization of carbonyl compounds. To achieve this aim *N*-halo compounds have been used widely as versatile reagents. Recently a broad range of *N*-halosulfonamides (NHSs) has been reported for regeneration of carbonyl compounds from oximes (Scheme 105) [130,131,135-139].

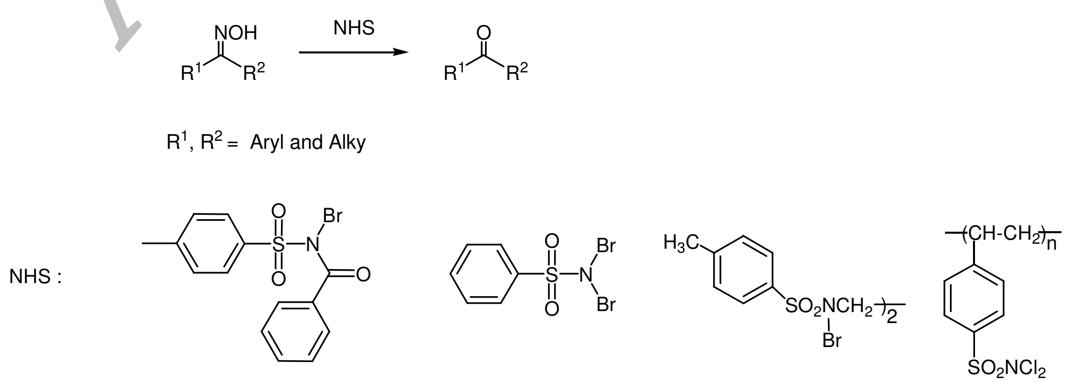
N,N´-Dibromo-*N,N´*-1,2-ethanediyl bis(*p*-toluenesulfonamide) (BNBTS) has catalytically been applied for tetrahydropyranylation of a various range of alcohols and phenols in dichloromethane and tetrahydropyranylation of these compounds has been also carried out in methanol at room temperature (Scheme 106) [140].

Scheme 106

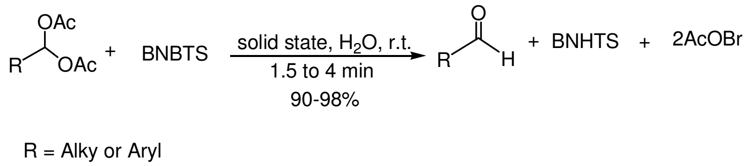
Conversion of 1,1-diacetates to aldehydes has been described using BNBTS in high yield and short time at room temperature under solvent-free condition (Scheme 107) [141].

Deprotection of 2,4-dinitrophenylhydrazones to their corresponding carbonyl compounds have been reported in good yields with BNBTS under microwave irradiation (Scheme 108) [142].

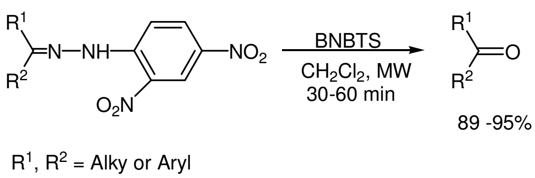
BNBTS has been used for deprotection of aliphatic and aromatic 1,3-dithianes to their corresponding carbonyl compounds under mild condition (Scheme 109) [143].



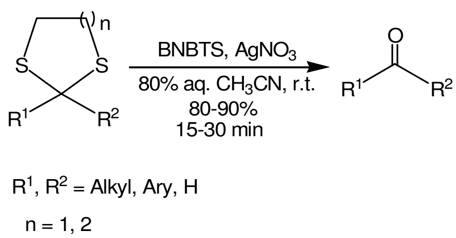
Scheme 105



Scheme 107

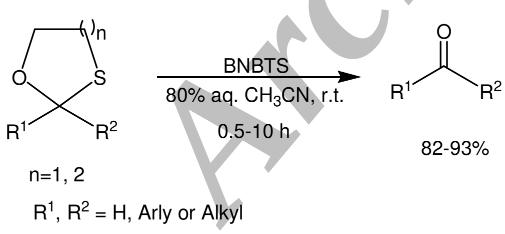


Scheme 108



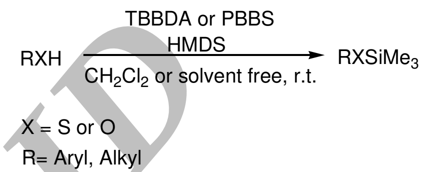
Scheme 109

Deprotection of 1,3-oxathiolanes to carbonyl compounds has been carried out with BNBTS in good yields under mild conditions (Scheme 110) [144].



Scheme 110

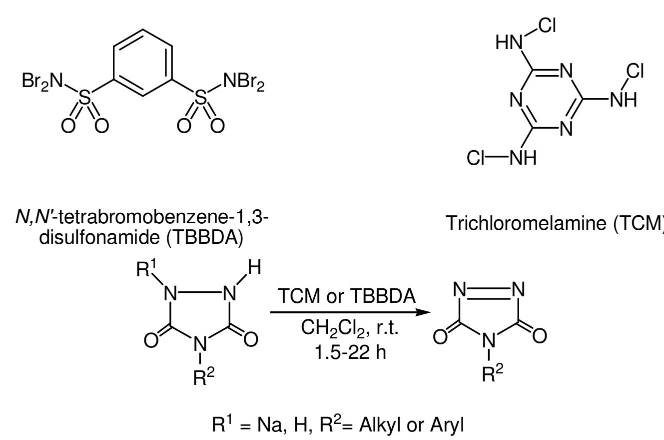
Poly(*N*-bromobenzene-1,3-disulfonamide) (PBBS) and *N,N,N′,N′*-tetrabromobenzene-1,3-disulfonamide (TBBDA) were reported as efficient catalysts for the silylation of alcohols, phenols, and thiols in the presence of HMDS under various conditions (Scheme 111) [145]. Since there are few reports on the silylation of thiols in the literature, the method is suitable and practical for this purpose.



Scheme 111

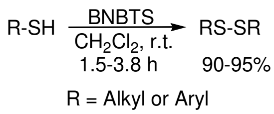
Oxidation Reactions

Another important application of *N*-halo reagents in organic chemistry is the oxidation of different functional groups through the release of halonium ions. TBBDA and TCM were used as effective oxidizing agent for the conversion of urazoles and bis-urazoles to the corresponding triazolinediones under mild and heterogenous condition at room temperature with good to excellent yields (Scheme 112) [146].



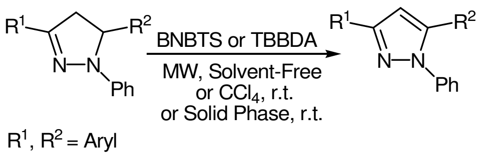
Scheme 112

Efficient oxidative coupling of thiols has been made by BNBTS for production of the corresponding disulfides at room temperature with good to excellent yields (Scheme 113) [147].



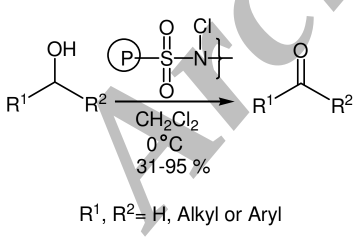
Scheme 113

N,N,N',N'-tetrabromobenzene-1,3-disulfonamide (TBBDA), BNBTS and PBBS were used as efficient reagents for the oxidation of 1,3,5-trisubstituted pyrazolines to their corresponding pyrazoles in solvent-free conditions both under microwave irradiation or at room temperature (Scheme 114) [148-151].



Scheme114

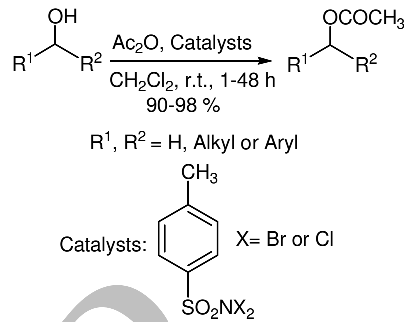
Poly(*p*-*N*-chlorostyrenesulphonamide) was used as an efficient polymeric oxidizing reagent for oxidation of primary and secondary alcohols to corresponding carbonyl compounds in the presence of DMSO in reasonable yields (Scheme 115) [152].



Scheme 115

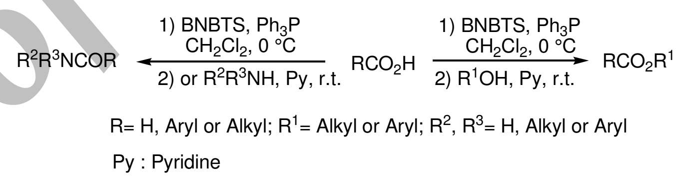
Miscellaneous Reactions

N-halo reagents have been also applied as catalyst in esterification reactions. *N,N*-dibromo(*p*-toluenesulfonamide) and *N,N*-dichloro(*p*-toluenesulfonamide) catalyze acetylation of structurally drivers alcohols by the reaction of acetic anhydride in chloroform at room temperature (Scheme 116) [153-154].

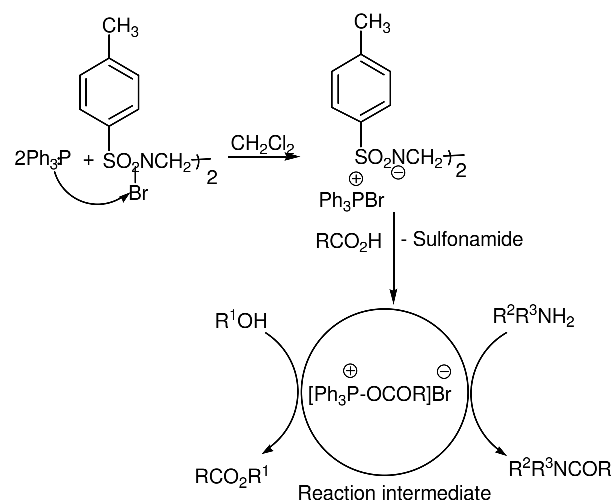


Scheme 116

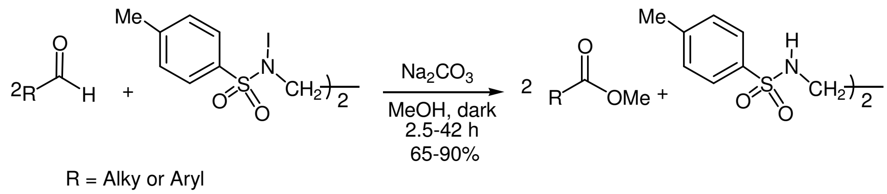
A combination of equal amount of Ph_3P and BNBTS has been used for the conversion of carboxylic acids into esters and amides in the presence of alcohols and amines, respectively (Scheme 117) [155]. Authors have suggested that the reaction is initiated *via* nucleophilic attack of triphenylphosphine to *N*-bromosulfonamide, followed by nucleophilic attack of alcohol or amine that afforded the corresponding esters or amides (Scheme 118).



Scheme 117



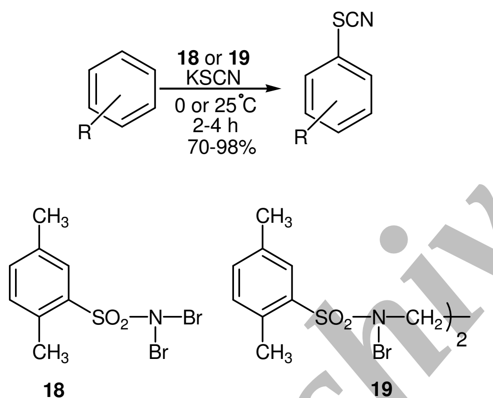
Scheme 118



Scheme 119

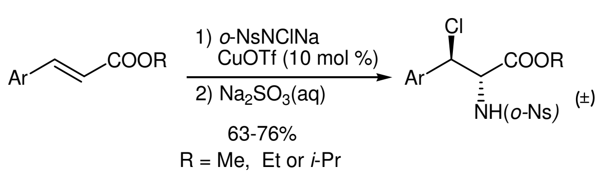
N,N´-Diiodo-*N,N´*-1,2-ethanediylbis(*p*-toluensulfonamide) (BNIBTS) has converted aldehydes to methyl esters in the presence of methanol in good yields at room temperature (Scheme 119) [156].

N-Bromosulfonamides **18** and **19** reacted with several types of arenes in the presence of KSCN at 0 or 25 ºC to afford aryl thiocyanates (Scheme 120) [157].



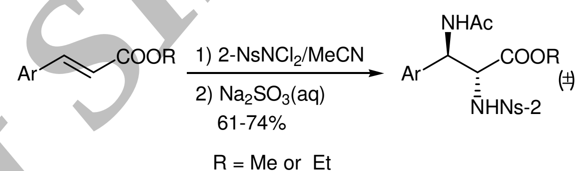
Scheme 120

A variety of olefins have been reacted with *N*-chloro-*N*-sodium-2-nitrobenzenesulfonamide (*o*-NsNClNa) in the presence of catalytic amounts of copper triflate to give vicinal halo amines stereoselectively (Scheme 121) [158].



Scheme 121

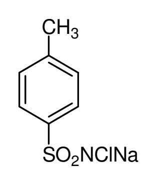
Tandem diamination of cynamic esters have been successfully carried out with *N,N*-di-chloro-2-nitrobenzene-sulfonamide (2-$NsNCl_2$) as a nitrogen source in acetonitrile. The corresponding diamine derivatives were stereoselectively obtained with good yields (Scheme 122) [159].



Scheme 122

CHLORAMINE T

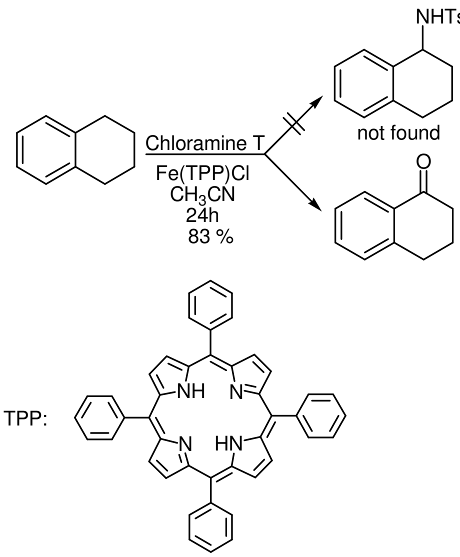
Sodium *N*-chloro-*p*-toluenesulfonamide, Chloramine T **20**, has diverse chemical properties. It is a commercially available, inexpensive, water-tolerant, non-toxic and easy to handle chemical. Chloramine T acts both as a source of 'halonium ion' as well as a 'nitrogen anion'. As a result, it reacts with a wide range of functional groups, leading to an array of molecular transformations. Chloramine T has been used in various types of chemical transformations such as aminohydroxylation, aminochalcogenation of alkenes, allylic aminations, and aziridinations [160].



20

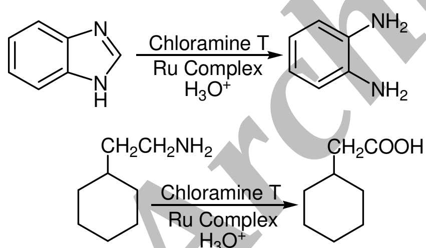
Wang and Li carried out oxidation of hydrocarbons to their corresponding ketones using the Fe(TPP)Cl/Chloramin T/O_2

system (Scheme 123) [161].



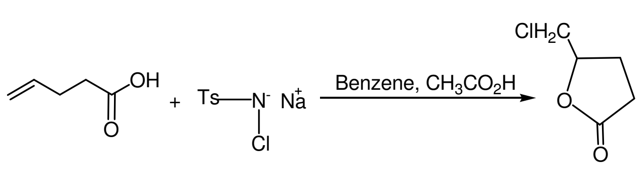
Scheme 123

Chloramine T was used for the conversion of some amines and imidazoles to corresponding oxidized compounds under catalytic conditions (Scheme 124) [162,163].



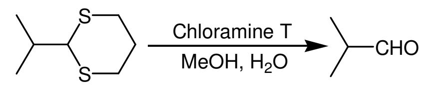
Scheme 124

Synthesis of chlorolactones by reaction of unsaturated carboxylic acids with Chloroamine T has been reported (Scheme 125) [164].



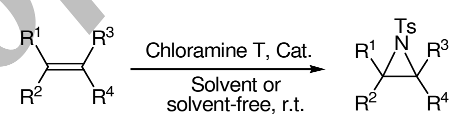
Scheme 125

Chloroamine T reacted with a variety of 1,3-dioxathiolanes and 1,3-dithiolanes and cleaved them to the original carbonyl compounds (Scheme 126) [165].



Scheme 126

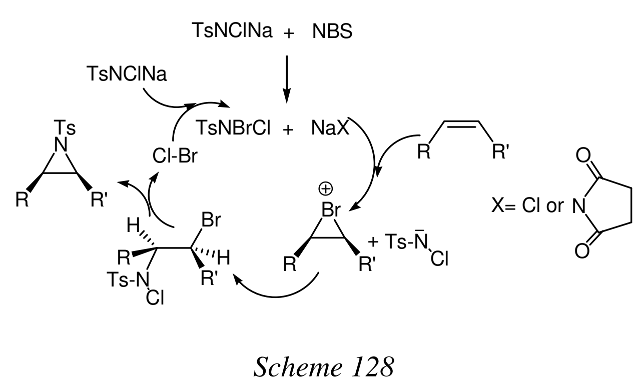
Aziridine, an important three-membered heterocyclic ring system, is a useful precursor for the synthesis of several biologically important compounds such as amino acids, amino sugars and alkaloids. For this purpose Chloramine T has been used in the presence of various catalysts (Scheme 127) [166-172].



Solvent: CH_3CN or H_2O
Catalyst:HPA/CTAB/MS 5 A°, Py/HBr_3, I_2/BTEAC, CuI/Ptc, MPHT or NBS
R^1, R^2, R^3, R^4 = Alkyl or Aryl
MPHT = *N*-methylpyrrolidine-2-one hydrotribromide

Scheme 127

Although mechanistic aspects of the aziridination have not been yet cleared, Sudalai *et al.* have suggested an interesting mechanism for aziridination in the presence of NBS as catalyst (Scheme 128) [167].



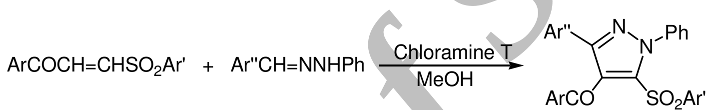
Scheme 128

2-Pyrazoline and 2-isoxazolines have been prepared by the reaction of araldehyde hydrazones and aldoximes with bifunctional olefins in the presence of Chloramine T. The generated 2-pyrazolines were also oxidized to the corresponding pyrazoles in the course of the reaction (Scheme 129) [173].

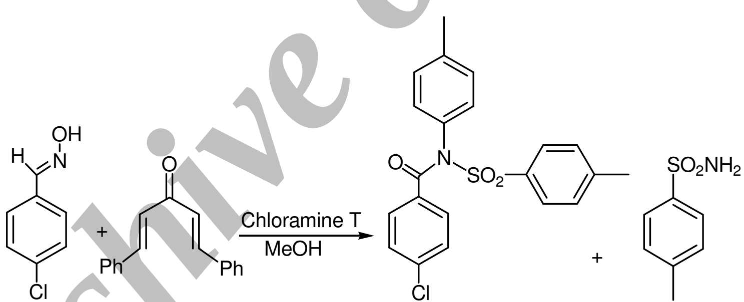
Reaction of araldoximes with 4 eq. of Chloramine T in refluxing methanol in the presence of 1,5-diphenyl-1,4-pentadien-3-one, produced *N*-(*p*-tolyl)-*N*-(*p*-tosyl)-benzamide *via* addition of 2 eq. Chloramine T to the intermediate followed by extrusion of sulfur dioxide. The 1,5-diphenyl-1,4-pentadien-3-one remained intact in the course of reaction (Scheme 130) [174]. Minakata *et al.* reported a new synthetic procedure for the amino chlorination of a variety of olefins and conjugated dienes to obtain vicinal chloramine derivatives with a combination of Chloramine T and carbon dioxide (Scheme 131) [175].

BROMAMINE T

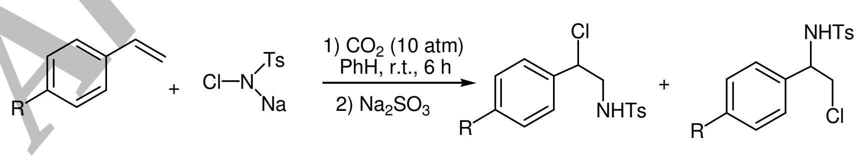
Bromamine T is the brominated analogue of Chloramine T. It has been used for aziridination of olefins in the presence of palladium (Scheme 132) [176]. The proposed mechanism is



Scheme 129



Scheme 130

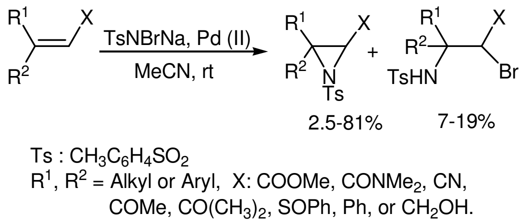


21 **22**

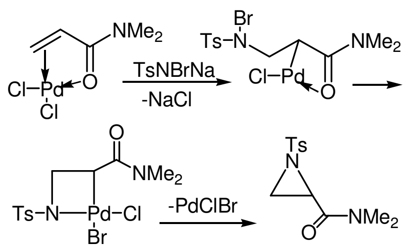
Entry	R	Yield (%)	
		21	**22**
1	NO_2	(21a) 71	(22a) 0
2	Cl	(21b) 74	(22b) 0
3	Me	(21c) 54	(22c) 9
4	MeO	(21d) 0	(22d) 76

Scheme 131

shown in Scheme 133.

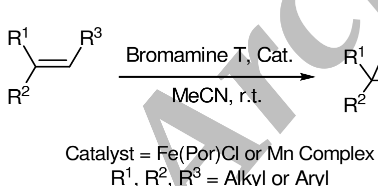


Scheme 132



Scheme 133

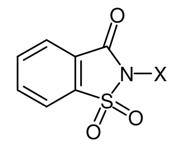
Both Fe(II) and Mn-porphyrin complexes are effective catalysts for aziridination of alkenes using Bromamine T, the reaction proceeded with moderate to low stereospecificity (Scheme 134) [177,178].



Scheme 134

N-HALOSACCHARINES

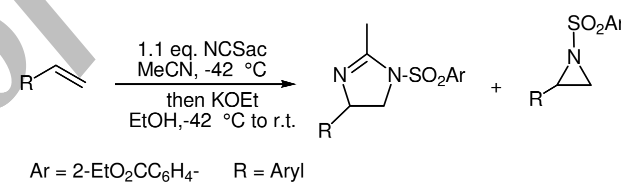
N-halosaccharines proved to be useful and alternative reagents for diverse organic transformations, such as halogenation of aromatic compounds, co-halogenation of alkenes, oxidation of alcohols, halogenation of benzylic and α-carbonylic positions, *etc*. *N*-Chloro-, *N*-bromo- and *N*-iodosaccharin, **23** (NCSac, NBSac, and NISac, respectively) are prepared easily starting from saccharin [179].



X= Cl, Br, I

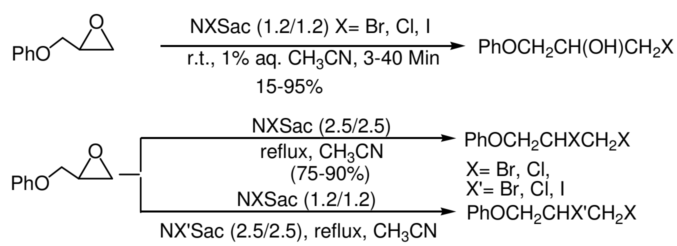
23

NCSac has been shown to undergo electrophilic-Ritter type reaction with alkenes in acetonitrile. These reactions have been carried out at -42 ºC up to room temperature and two different products have been obtained (imidazoline or aziridine) (Scheme 135) [180].



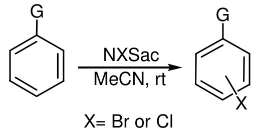
Scheme 135

N-halosaccharines have been used for regioselective cleavage of epoxides into vicinal halohydrins and dihalides in the presence of Ph_3P (Scheme136) [181].



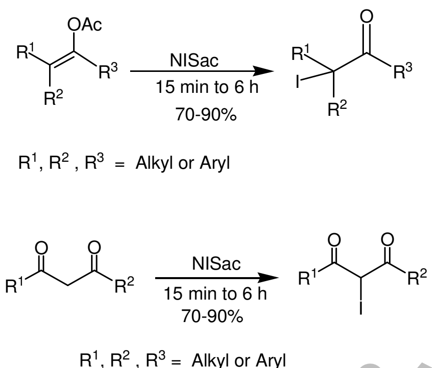
Scheme136

Chlorinated and brominated aromatic compounds were prepared selectively by reaction of electron-rich aromatic compounds with NCSac or NBSac in good yields at room temperature (Scheme 137) [182].



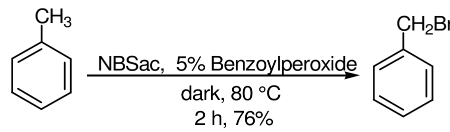
Scheme 137

Dolenc reported iodination of enole acetates and 1,3-diones with NISac yielding the corresponding α-iodoketones and 2-iodo-1,3-diones (Scheme 138). Reactions were carried out at room temperature under neutral condition in good yields and short reaction times [183].



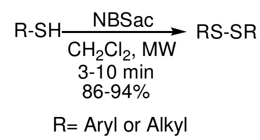
Scheme 138

Sanchez and Fumarola reported an efficient method for benzylic and α-carbonylic bromination using NBSac under mild conditions (Scheme 139) [184].

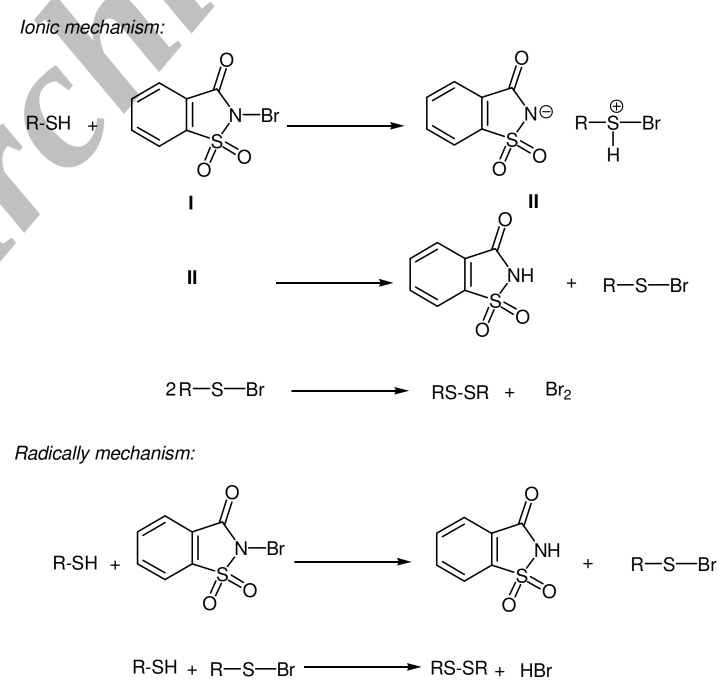


Scheme 139

NBSac has successfully been used for chemoselective oxidation of thiols to their corresponding disulfides in dichloromathane under microwave irradiation in high yields (Scheme 140) [185]. Two mechanisms were proposed for these reactions that both are shown in scheme 141.

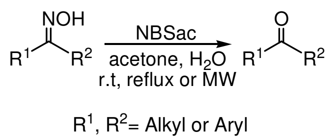


Scheme 140



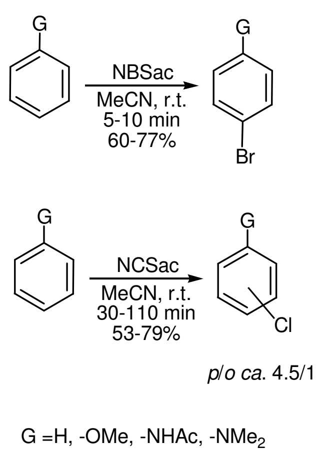
Scheme 141

NBSac was applied as an efficient reagent for the oxidative cleavage of oximes to the corresponding aldehydes and ketones under microwave irradiation with reasonable yields [186]. The same group has reported the above transformation with NBSac in water and acetone as solvent at room temperature or by conventional heating or microwave irradiation (Scheme 142) [187].



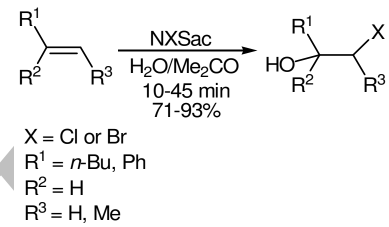
Scheme 142

NCSac and NBSac were successfully applied for halogenation of electron rich aromatic compounds (anisole, acetanilide, *N*,*N*-dimethylaniline) [188]. The reaction with NBSac gave *para*-substituted compounds only, whereas NCSac produced a mixture of *ortho* and *para* isomers (Scheme 143).



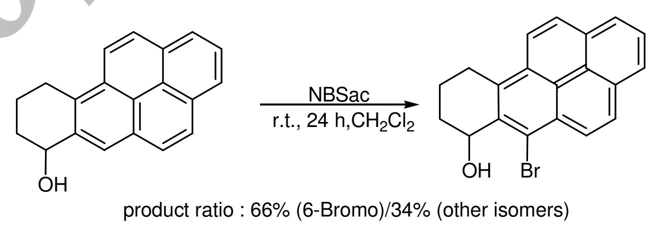
Scheme 143

The reactions of NCSac and NBSac with alkenes (cyclohexene, styrene, α-methylstyrene, and 1-hexene) gave the corresponding halohydrins in H_2O and acetone as solvent (Scheme 144) [188].



Scheme 144

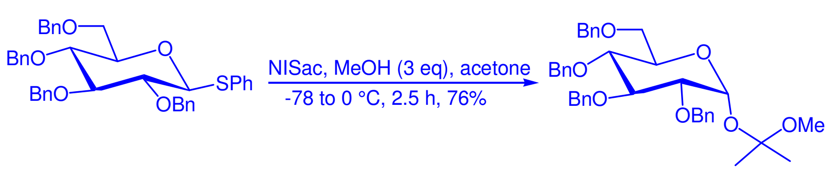
Bromination of 7,8,9,10-tetrahydrobenzo[*a*]pyren-7-ol was selectively carried out with NBSac (Scheme 145) [189].



Scheme 145

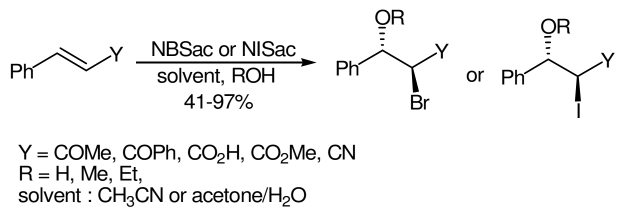
Aloui and Fairbanks have reported glycosylation reactions by NISac in the presence of acetone and methanol for stereoselective production of acetal-linked α-glycosides (Scheme 146) [190].

NBSac and NISac reacted with electron-deficient alkenes such as α,β-unsaturated ketones, acids, esters and nitriles in aqueous organic solvents, yielding the corresponding halohydrins in good yields (Scheme 147) [191]. The reactions



Scheme 146

took place at room temperature, mostly within short reaction times and with high *anti* stereoselectivity.



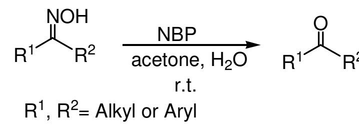
Scheme 147

N-HALOPHTHALIMIDES

N-Halophthalimides (NXP) have been used in organic synthetic methodology especially in the oxidation and bromination reactions. In most cases these reagents are converted to phthalimide in the end of reactions, as a nontoxic chemical.

N-Bromophthalimide

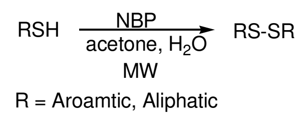
N-Bromophthalimide (NBP) has been found to be an efficient and selective reagent for the mild oxidative cleavage of oximes to yield the corresponding carbonyl compounds in good to excellent yields (Scheme 148) [192].



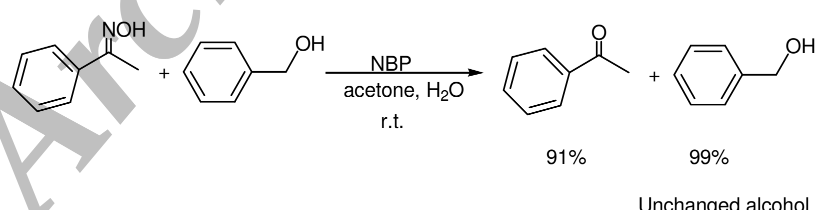
Scheme 148

An interesting example of the chemoselectivity of these reactions includes deoximation in the presence of primary benzylic alcohols (Scheme 149).

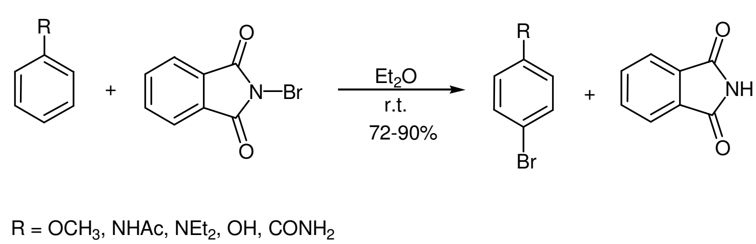
Similar reactions were also carried out under microwave irradiation in very short times [193]. NBP has been used for the oxidation of various organic compounds in the presence of mercuric acetate as well as in acetic acid medium. Among them, kinetic studies were carried out for the oxidation of glycylglycine [194], aromatic aldehydes [195,196], acetophenone derivatives [197,198], aliphatic amines [199], α-hydroxy acids [200], and aspirin [201]. NBP was used for the facile oxidation of thiols to symmetrical disulfides in a mixture of acetone-water under microwave irradiation [202]. Both aromatic and aliphatic thiols were selectively oxidized in good to excellent yields (Scheme 150).



Scheme 150



Scheme 149

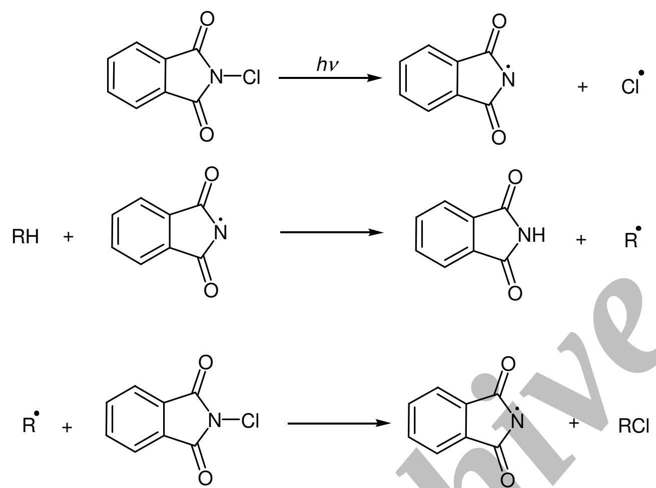


Scheme 151

Reaction of substituted benzene rings with NBP, under neutral conditions, gave the corresponding bromo derivatives with a preference for the formation of *para* over the *ortho* isomers (Scheme 151) [203]. NBP has also been used for the bromination of some deoxyhexoses [204].

N-Chlorophthalimide

The photoinitiated free radical chlorination of hydrocarbons with *N*-chloro-phthalimide (NCP) has been reported [205]. Some evidence led authors for the suggestion of the chlorination mechanism (Scheme 152).

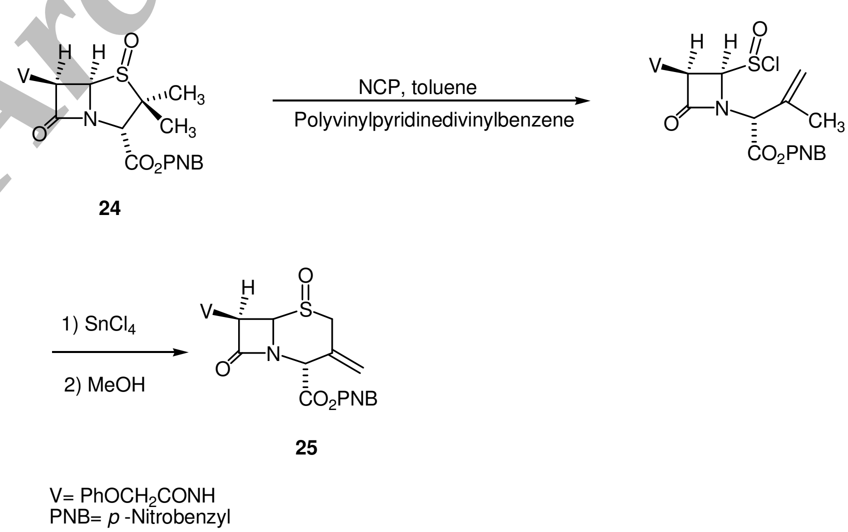


Scheme 152

NCP was successfully used in the first step of the ring expansion of peniciline V sulfoxide *p*-nitrobenzyl ester **24** to 3-exomethylene cephalosporin V sulfoxide *p*-nitrobenzyl ester **25** (Scheme 153) [206].

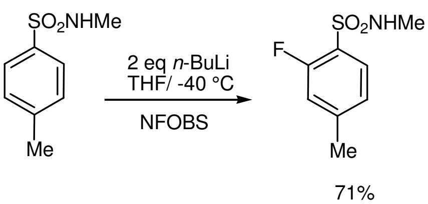
N-FLUORO REAGENTS

The development of mild and selective methods for introduction of fluorine into organic substrates is an important objective because this element exerts unique influences upon physical, chemical, and biological properties. Until quite recently, however, the selective electrophilic fluorination of enolates and carbanions was difficult because most procedures employed highly reactive, corrosive and toxic materials such as F_2, $FC1O_3$, or $MeC(O)CF_3$. To overcome these limitations, a range of *N*-fluoro reagents with different reactivities, that were safe and easy to handle without special equipment, was developed [207]. These reagents are easy to handle but have low reactivity [208]. Recently, fluorous biphasic and triphasic systems has been developed so that catalysts which has perfluoroalkyl groups as tags are soluble in perfluoro solvents and insoluble in virtually all common organic solvents [209,210]. We think that *N*-fluoro reagents may be effectively used in the above mentioned systems in future. Several reviews concerning *N*-fluoro reagents have been published [211,213]. Therefore in this article some recent applications of



Scheme 153

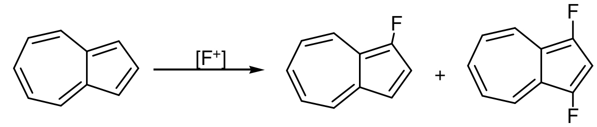
N-fluoro reagents are reviewed. Sniekus *et al.* have reported flouroniation of aromatic compounds by *N*-fluorobenzensulfonimide (NFSi) and *N*-fluoro-*o*-benzenesulfonamide (NFOBS) *via* direct ortho metallation (Scheme 154) [214].



Scheme 154

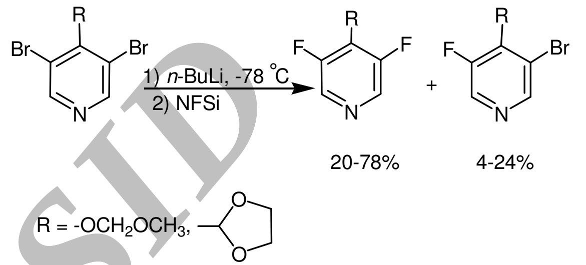
Hiyakawa *et al.* have reported fluorination of indols using NFSi and a directed metallation group (Scheme 155) [215].

1-Fluoro- and 1,3-difluoroazulenes were synthesized for the first time by the electrophilic fluorination of azulenes with *N*-fluoro reagents such as NFSi, *N*-fluoro pyridinium salts, selectfluor and accufluor (Scheme 156) [216].



Scheme 156

NFSi has been applied for the synthesis of novel 3,5-difluoropyridine-4-carboxaldehyde in good to high yields at -120 ºC to -78 ºC. Maintaining the low temperature during the trans metallation was found to be critical for the selective formation of difluoro over monofluoro derivatives (Scheme 157) [217].

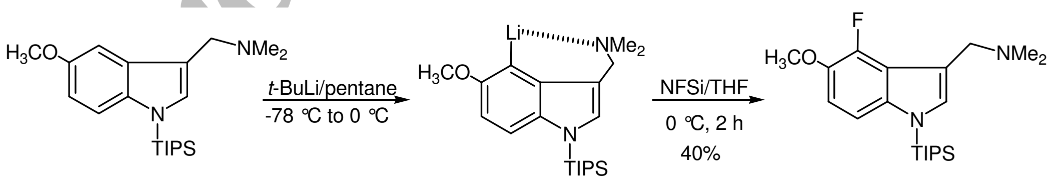


Scheme 157

Laulo *et al.* have shown that *N*-fluoro-2,4-dinitroimidazole can fluorinate several classes of polycyclic aromatic hydrocarbons (PAHs) (Scheme 158) [218].

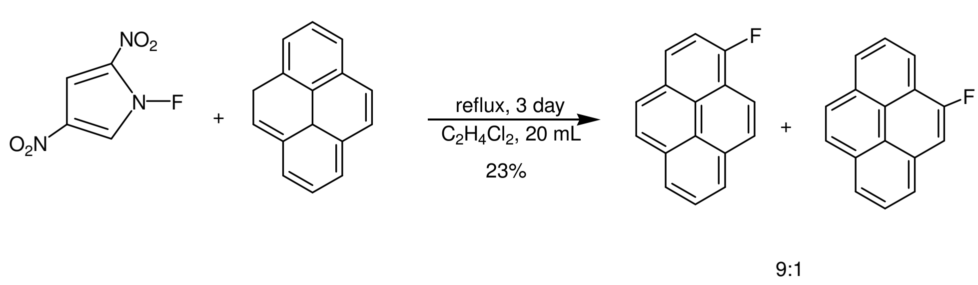
Banks *et al.* reported preparation of some *N*-fluoro reagents [219-221]. These reagents have been used for fluorination of various organic compounds (Scheme 159).

A regioselective method for the fluorination of dibenzofuran diphenylether and biphenyl with different *N*-fluoro reagents has also been reported [222]. A typical example for fluorination of dibenzofuran by three different

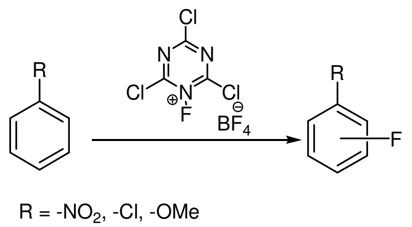


TIPS = triisopropylsilylgramine

Scheme 155



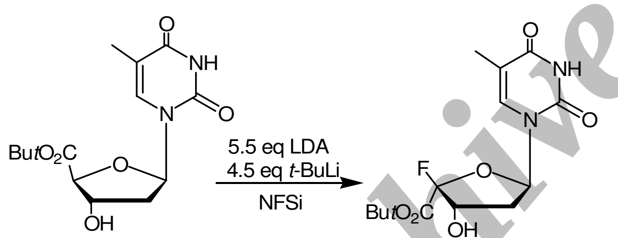
Scheme 158



Scheme 159

N-fluoro reagents is shown in Scheme 160.

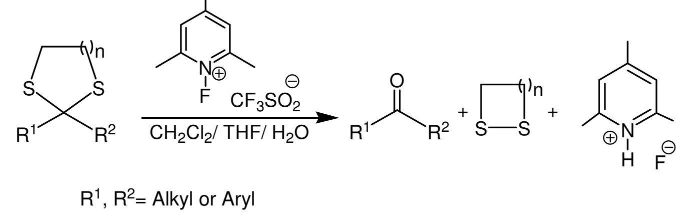
Modified nucleosides have become useful agents for the treatment of cancer and viral diseases due to their good antitumor and antiviral activity. In particular, several nucleosides with substituents at 4'-position are good candidates as antiviral agents. 4'-Fluoro nucleoside is one of these moieties that have strong activity including anti-HIV activity. Jung and Toyota have synthesized 4'-fluorothymidines using NFSi as fluorinating agent (Scheme 161) [223].



Scheme 161

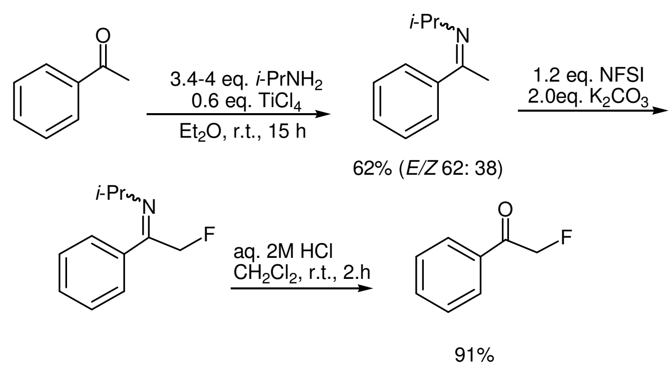
N-Fluoro-2,4,6-trimethylpyridinium triflate efficiently cleaved dithioacetals to the parent carbonyl compounds (Scheme 162) [224].

An important application of *N*-fluoro reagents is fluorination of activated methylene [225-237] and enolate

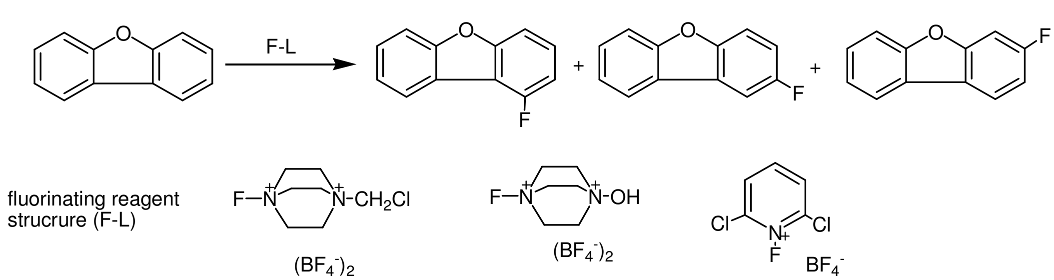


Scheme 162

groups [238-239] to achieve a broad range of α-fluorinated organic compounds such as α-fluorosulfonamides, α-fluorolactams, α-fluoroketones, *etc*. Various *N*-alkylimines derived from acetophenones were successfully monofluorinated using NFSi in a mixture of acetonitrile and DMF at 0 ºC. Alternatively, the same procedure in the absence of DMF gave rise to diflourinated imines when performed at room temperature. The obtained α-fluoro and α,α-difluoro-imines were subsequently reduced to give the corresponding β-flouro and β,β-diflouroamines (Scheme 163) [237].



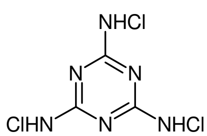
Scheme 163



Scheme 160

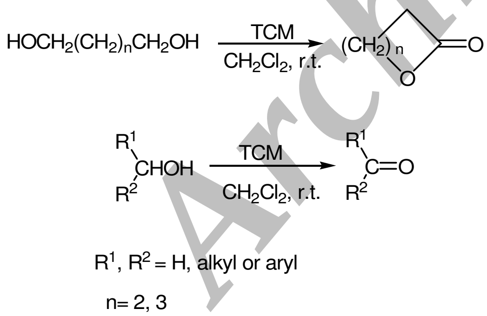
N-HALOAMINES

There are few papers concerning the utilization of *N*-halo amines in organic synthesis. Generaly *N*-halo amines can be viewed as a source of halonium ions. There are only few *N*-halo amines such as trichloromelamine and *N,N*,2,3,4,5,6-heptachloroaniline that can be used as a chloronium ion source. Trichloromelamine (TCM, **26**), is a source of chloronium ion because the 1,3,5-triazine ring has strong electron-withdrawing character. However, there are few papers concerning the utilization of TCM in organic synthesis [240-241].



26

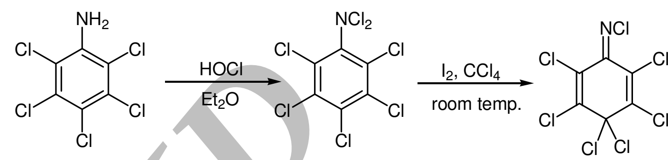
Kondo *et al*. have reported a simple and selective method for the oxidation of alcohols to the corresponding carbonyl compounds and oxidative lactonization of diols with TCM in methylene chloride at room temperature under mild conditions (Scheme 164) [242].



Scheme 164

N,N,2,3,4,5,6-Heptachloroaniline **27** and *N*-chloro-2,3,4,4,5,6-hexachlorocyclohexa-2,5-dienylideneamine **28** (Scheme165) can be used as chlorinating agents. Compound **28** was used as a new mild and highly regioselective chlorinating reagent in the chlorination of phenol and *o*-cresol in CCl_4, DMF and CH_3CN. The effects of C_2H_5OH, C_5H_5N, DMF, and Et_3N on the regioselectivity in CCl_4 have been examined [243].

Oxidation of urazoles and bis-urazoles was carried out with **27**. The *in situ* generation of Cl^+ appeared to be vital for the oxidation of urazoles using this reagent [244].

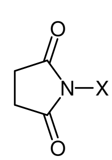


27 **28**

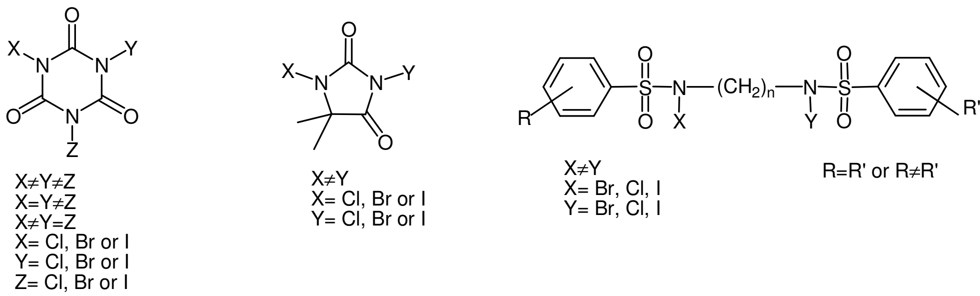
Scheme 165

N-HALOSUCCINIMIDE

Some specific properties of *N*-halosuccinimides (NBS, NCS and NIS) cause their wide application in organic synthesis. The scope of the application of *N*-halosuccinimides is so wide that needs a special review for covering their chemistry. The recent application of NBS as a catalyst, oxidant, selective brominating reagent and the initiator in the polymerization has been reviewed [245]. Although two excellent review articles have been published on this subject [1,245] we think that publishing a new review for covering the new applications of these compounds in organic synthesis is necessary. *N*-Hallosuccinimides are commercially available and extensively had been used in many fields of fine organic synthesis and at natural compounds chemistry as well [1]. Therefore, due to the above mentioned facts we decided to avoid reviewing the recent application of *N*-halosuccinimides in the present manuscript. However, we are preparing a review article on this subject that will be published in near future.



NBS: X=Br
NCS: X=Cl
NIS: X=I



Scheme 166

CONCLUSIONS

It should be noted that a correct and updat citation and literature survey is very important for researchers to find relevant information, pioneer ideas, and progress of any subject. On the other hand, published data using *N*-halo reagents indicate a wide synthetic potential of the described reagents and a great interest of researchers in these compounds. A wide range of original procedures for synthesizing various classes of organic compounds, including organic functional group transformation have been developed on the basis of *N*-halo reagents. We think that the present review article may be bringing a basic to advance information to this very important subject and to encourage active researchers in this field for the synthesis of new *N*-halo reagents with different halogens such as those given in Scheme 166.

ACKNOWLEDGMENTS

The authors thank their coworkers, named in the references, for their experimental and intellectual contributions.

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