Nitro and related compounds

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Reviewing the literature published between December 1993 and May 1995

1 Introduction

This review covers not only the recent advances in the synthesis of nitro compounds and related derivatives, but also indicates the main current areas of interest in the properties of such compounds, both chemically and biologically.

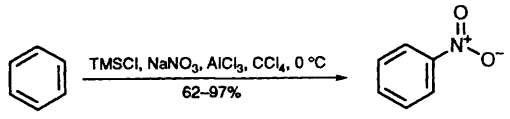
2 Nitro compounds

A review of the most expedient reactions and conversions of aliphatic and aromatic nitro compounds for organic synthesis has recently been published.[1]

2.1 Aryl nitro compounds

Primary anilines can be oxidized to the corresponding nitro compounds under very mild conditions using oxone (potassium peroxymonosulfate) in 5 to 20% aqueous acetone, buffered with sodium bicarbonate.[2]

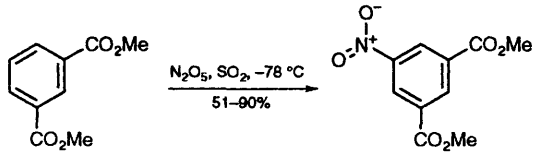
A mixture of sodium nitrate and TMSCl has been developed as a convenient method for the *in situ* generation of nitryl chloride. In combination with complexation with a Lewis acid, such as aluminium trichloride, this forms a convenient system for the nitration of aryl rings (**Scheme 1**).[3] Nitryl chloride was previously prepared by either the oxidation of nitrosyl chloride, or by the reaction of chlorosulfonic acid with nitric acid. However, both these earlier methods are rather inconvenient and also potentially dangerous. The utilization of the reaction of TMSCl with sodium nitrate for the *in situ* generation of nitryl chloride is therefore a distinct improvement.



Scheme 1

Aromatic compounds can be nitrated with HNO_3 under mild non-corrosive conditions, by co-treatment with an activated mixture of a metal nitrate modified silicate and TFAA in CH_2Cl_2. Polynitration can also occur depending both on the nature of the substrate and the conditions employed.[4]

Dinitrogen pentoxide in liquid sulfur dioxide has been developed as a new nitration system with wide potential for the nitration of aromatic systems, including deactivated rings (**Scheme 2**).[5] The resulting aryl nitro compounds are formed with similar substitution patterns to those observed in 'traditional' nitrations with HNO_3/H_2SO_4.

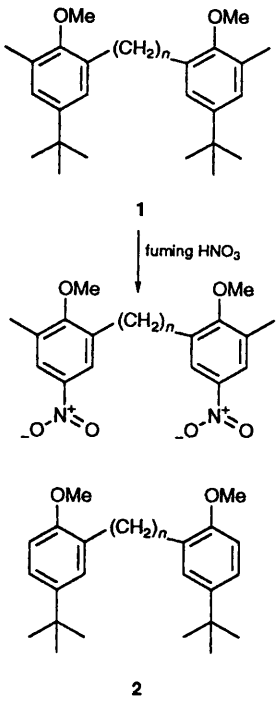


Scheme 2

Some heteroaromatic rings, such as pyridines and quinolines, can also be nitrated with this system, but others such as pyrimidines, pyrroles, imidazoles, or indoles are not nitrated under these conditions.[6]

The replacement of a t-butyl group by a nitro group in electrophilic substitution reactions is typically complicated by concomitant side-reactions. The replacement of a t-butyl group via *ipso*-electrophilic substitution of t-butylarenes is, however, possible for activated aryl rings where the initial σ-complex has increased stabilization.[7] For example, biaryl compounds of the type **1** undergo clean *ipso*-nitration, whilst the less substituted analogues **2** undergo simultaneous nitration at the position *ortho* to the anisole group (**Scheme 3**).

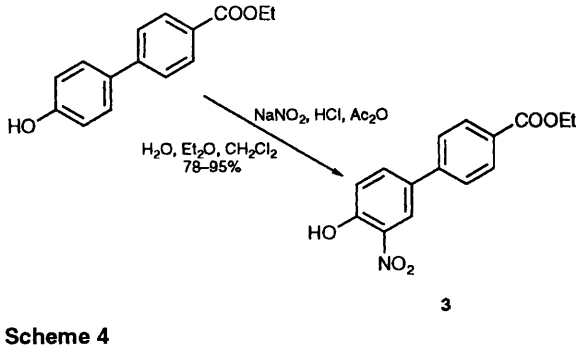
The orientation of electrophilic substitution, including nitration, of benzaldehydes can be changed selectively by the prior conversion of the aldehyde group into the corresponding *O*-ethyloxyoxime. Thus, whilst nitration of benzaldehyde gives a mixture of the *ortho*- and *meta*-isomers, treatment of the corresponding *O*-alkyl oxime with nitric acid



Scheme 3

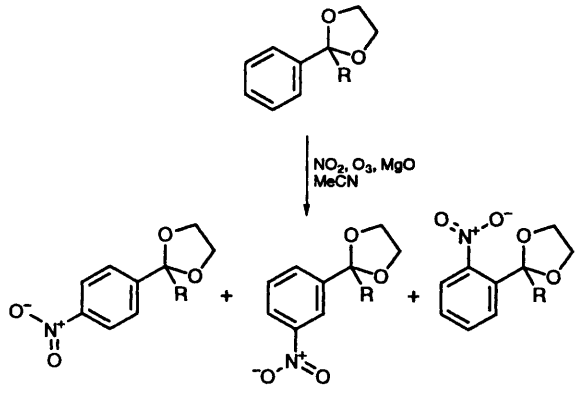
in sulfuric acid gives selectively the *meta*-isomer in high yield.[8]

An efficient two-phase nitration of *para*-substituted phenols has been developed. Thus, *para*-substituted phenols are readily *ortho*-nitrated at room temperature by treatment with sodium nitrate in a 2-phase aqueous/organic system, in the presence of HCl and a catalytic amount of acetic anhydride. This protocol has been applied to the nitration of biaryl compounds, such as **3** (**Scheme 4**).[9]



Scheme 4

Nitrogen dioxide, in the presence of ozone, is a good nitrating agent for aromatic systems. The active nitration reagent is probably *in situ* generated dinitrogen pentoxide. This novel nitration method has become known as the 'kyodai-nitration' and is suitable for the nitration of nonactivated and even deactivated aromatic compounds into the corresponding mono- or poly-nitro derivatives in good to excellent yields. Even acid-sensitive aromatic compounds, such as benzaldehyde acetals, can be nitrated under neutral conditions via this ozone-mediated reaction of the aromatic compound with nitrogen dioxide by carrying out the reaction in the presence of magnesium oxide.[10] However, the reaction is limited to cyclic acetals and provides a mixture of isomeric nitro compounds in which the *para*- and *ortho*-isomers predominate (**Scheme 5**). The related acylal is also nitrated under these conditions, but in contrast gives mostly the *ortho*- and *meta*-isomers.



Scheme 5

The regioselectivity of the kyodai-nitration process differs from that of conventional nitration such that, for example, substrates bearing an electron-withdrawing group are preferentially nitrated in the *ortho*-position. Thus alkyl aryl ketones react smoothly with nitrogen dioxide at low temperatures in the presence of ozone to give *ortho*- and *meta*-nitro derivatives, with a limited preference, of up to 4:1, for the *ortho*-analogue.[11]

Controlled mononitration is also possible using modified conditions with nitrogen dioxide and ozone in the presence of methanesulfonic acid as catalyst; for example, polychlorinated benzenes undergo selective mononitration with this system.[12]

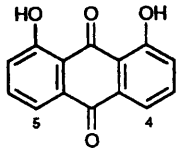
Ozone-mediated nitrogen dioxide nitration is also an effective method for the nitration of various benzoic acid derivatives (and the corresponding nitriles), yielding predominantly the *meta*-isomer.[13] Benzamide, however, is not nitrated but rather undergoes loss of the nitrogen to afford benzoic acid and its nitrated derivatives, whilst *N*,*N*-dialkylbenzamides are nitrated to mixtures of all three regioisomeric nitro compounds.

Finally, the kyodai-nitration process of ozone-mediated nitration of aromatic compounds has also been studied as an environmentally cleaner alternative to conventional nitration mixtures.[14] Hydroquinone ethers react with nitrogen dioxide in dichloromethane to give either the nitrated product or the product of oxidative dealkylation. The competition between these two processes can be controlled by the solvent polarity and added nitrate. Thus, with acetonitrile as solvent chemoselective nitration occurs, whilst in non-polar solvents, such as hexane, only oxidative dealkylation is observed.[15]

Michael condensation reactions involving *p*-nitrobenzyl sulfones containing carbonyl or cyano substituents *ortho* to the methylsulfonyl group and electrophilic olefins or alkynes as the acceptor moiety provide a facile and efficient route to substituted 2-nitronaphthalene derivatives.[16]

New synthetic routes to tetranitrotoluenes have been reported, including the previously unknown 2,3,4,5-tetranitrotoluene.[17] The methods employed include the peroxydisulfuric acid oxidation of trinitrotoluenes, and the hypophosphorus acid reduction of diazonium salts derived from tetranitrotoluenes.

Typically, direct nitrations of chrysazin **4** give a complex mixture of polynitrated products. A significantly improved method for the selective nitration of chrysazin to 4,5-dinitrochrysazin has been reported involving the addition of boric acid to the nitration mixture.[18]



4

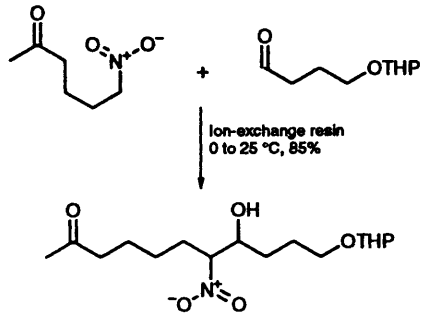
The nitration of toluene with n-propyl nitrate can be catalysed by the zeolite H-ZSM-5. The reaction proceeds in a regioselective manner to give the *ortho*-isomer preferentially.[19] The regioselectivity of the reaction can be controlled by the Si/Al ratio of the catalyst with high ratios, preferably 1000:1, favouring the formation of the *ortho*-isomer.

2.2 Alkyl nitro compounds

Alkenes react with nitrosyl chloride, generated *in situ* from TMSCl and sodium nitrite, to give α-chloro nitro compounds.[20]

The Henry reaction of nitroalkanes with aldehydes, leading to 2-nitroalkanols, can be catalysed by potassium-exchanged layered zirconium phosphate, $Zr(KOPO_3)_2$, as a base catalyst.[21] The reaction occurs under mild conditions at ambient temperature and without solvent. This protocol offers potential improvements over the 'classical' methods of preparation of 2-nitroalkanols, which often give poorer yields. However, the required zirconium catalyst must be prepared by titration of a zirconium phosphate.

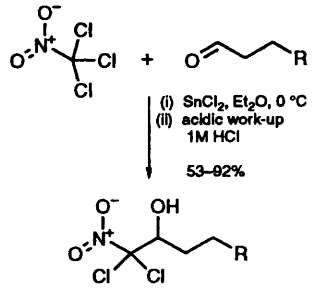
Asymmetric Henry reactions can be effected by the use of (*S*)-2,2′-dihydroxy-1,1′-binaphthyl in the presence of a lanthanum salt such as $La(Ac_3)_3$ and LiCl as catalyst.[22] Excellent chemical yields and high optical yields of 90% e.e. are obtained with this protocol. Henry reactions can also be promoted by ion-exchange resins such as Amberlyst-A21. These reaction conditions for the nitroaldol condensation are suitable for compounds containing acid-sensitive groups such as THP-protecting groups (**Scheme 6**).[23]



Scheme 6

2.3 α-Substituted nitro compounds

Reactions of aldehydes with trichloronitromethane in the presence of tin(II) chloride yield dichloronitro alcohols via a novel Reformatsky-type reaction (**Scheme 7**).[24] Aliphatic aldehydes react more efficiently and give higher yields than aryl aldehydes.

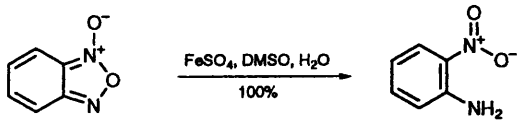


Scheme 7

α-Keto nitro compounds can be synthesized from the corresponding carbonyl compound by reaction in a two-phase system of the nitration mixture in $CHCl_3$ at −10 to +10 °C.[25] The utilization of a two-phase system avoids the formation of furoxanes as by-products and facilitates the work-up procedure.

Oxidative cross-coupling reactions of alkylated derivatives of activated CH compounds, such as malonic esters, acetylacetates, cyanoacetates, and some ketones, with nitroalkanes promoted by silver nitrate or iodine lead to the formation of the corresponding nitroalkylated products.[26] This reaction is of particular value for systems where the Kornblum reaction fails.

Reduction of benzofuroxan derivatives with iron sulfate in aqueous DMSO, or with thiophenol in the presence of a catalytic amount of an Fe^{2+} or Fe^{3+} salt, has been shown to provide *o*-nitroanilines in high yield (**Scheme 8**).[27]

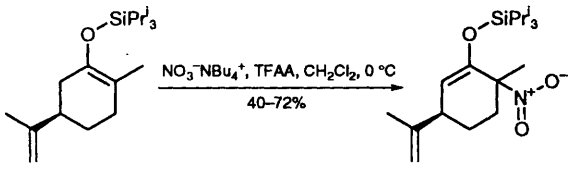


Scheme 8

Oxidations of α-amino esters with the HOF·MeCN complex (prepared by bubbling

fluorine gas through aqueous acetonitrile), provides a new route to α-nitro acids under mild conditions.[28] Moreover, although the HOF·MeCN complex can oxidize aromatic rings and especially activated systems, the rapid reaction times for its reaction with amino groups allow their selective oxidation in the presence of aromatic rings.

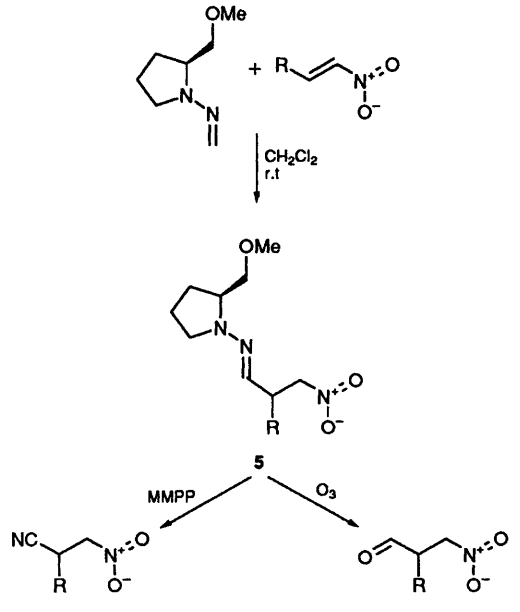
Triisopropyl silyl enol ethers are nitrated regioselectively at the most substituted carbon to give the corresponding α-nitro triisopropylsilyl enol ether via treatment with tetra-n-butylammonium nitrate and TFAA at 0 °C (**Scheme 9**).[29]



Scheme 9

Vicinal-dinitro compounds containing a nitrodioxane sub-unit can be obtained by the SR_{N1} reaction between either open-chain *gem*-chloronitro derivatives as substrates and an anion from nitrodiozane as the nucleophile and vice versa with the *gem*-chloronitrodioxane as the substrate. The former protocol is the more efficient as the reaction conditions are more readily tailored to the participating reagents.[30]

Functionalized nitro compounds such as the chiral β-nitrohydrazone **5** which can provide ready access to a variety of other functionalized systems (**Scheme 10**) are readily prepared via the non-catalysed Michael-type addition of formaldehyde SAMP hydrazone to nitroolefins.[31]



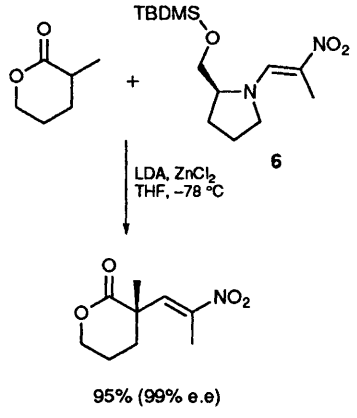
Scheme 10

2.4 α,β-Unsaturated nitro compounds

The relevant literature on the synthetic routes to, and the reactions of, nitroalkenes up to 1993, with a special emphasis on the recent literature, has been reviewed by Perekalin and his co-authors in their in-depth monograph.[32] This book should serve as an excellent source of information on the chemical transformations of nitroalkenes.

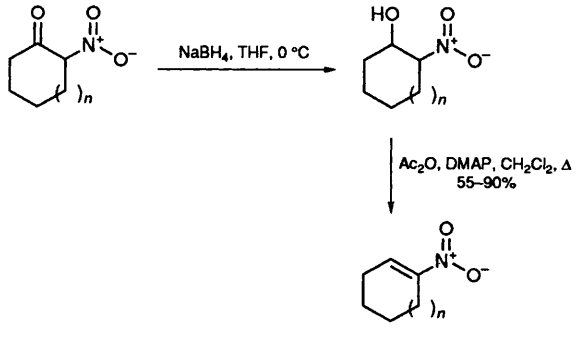
Alkenes can be nitrated in a regioselective manner to give the corresponding α,β-unsaturated nitroalkenes by sonication in a sealed tube at 25–73 °C of a $CHCl_3$ solution of the alkene, containing excess sodium nitrite and the cerium salt $Ce(NH_4)_2(NO_3)_6$.[33] The reaction occurs via the addition of a $NO_2^{\cdot}$ radical to the least substituted carbon atom; thus mono-substituted alkyl or aryl alkenes are nitrated exclusively on the vinylic carbon.

An improved asymmetric nitroolefination reaction of α-alkyl-γ-lactones and δ-lactones utilizes modified nitroenamines, such as **6**, as the nitro-transfer reagent. In these addition reactions zinc enolates were found to have enhanced reactivity over their lithium counterparts (**Scheme 11**).[34] High enantiomeric excesses are reported and presumably arise from chelation control in the transition state.[35]



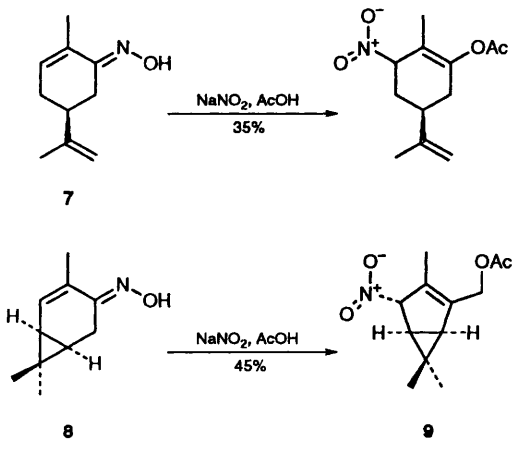
Scheme 11

A new one-pot procedure for the conversion of α-nitrocyclic ketones into α,β-unsaturated nitro olefins involves the $NaBH_4$ reduction of the ketone, followed by successive acetylation, and dehydroacetylation with basic alumina and DMAP (**Scheme 12**).[36]



Scheme 12

α,β-Unsaturated oximes can be converted into allylic nitrates via their reaction with sodium nitrite in acetic acid.[37] The reaction can occur either with retention or rearrangement of the carbon skeleton, depending on the substrate. For example, carvone oxime **7** undergoes nitration without skeletal rearrangement (**Scheme 13**), whilst car-2-en-4-one oxime **8** is nitrated with concomitant skeletal rearrangement to the cyclopentene **9**.



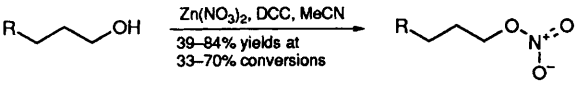
7 8 9

Scheme 13

3 Nitrate esters

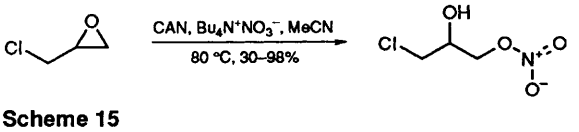
Nitrate esters can be prepared in moderate to high yields from the corresponding alkyl tosylates by treatment with sodium nitrate at 110–135 °C in a sealed tube using a two-phase benzene/water system, in the presence of tetrabutylammonium nitrate as catalyst.[38]

A mild and selective method for the conversion of primary and secondary alcohols into the corresponding nitrate esters is their treatment with zinc nitrate in the presence of DCC (**Scheme 14**).[39] Tertiary alcohols are unreactive under these conditions.



Scheme 14

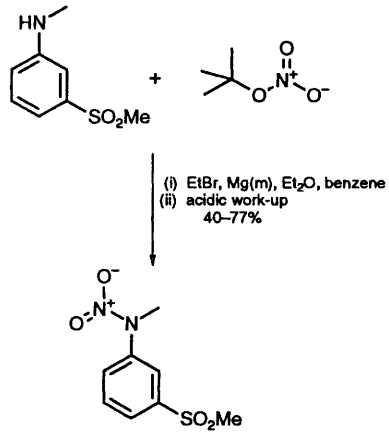
Catalytic amounts of ceric ammonium nitrate, either alone or in the presence of excess nitrate ion, react smoothly with epoxides under mild conditions to produce the corresponding β-nitrato alcohols (**Scheme 15**) through the intermediacy of an epoxonium radical cation which undergoes nucleophilic attack by the nitrate anion.[40] This procedure avoids the harsher and strongly acidic conditions previously used for the formation of β-nitrato alcohols from epoxides using nitric acid.



Scheme 15

4 Nitramines

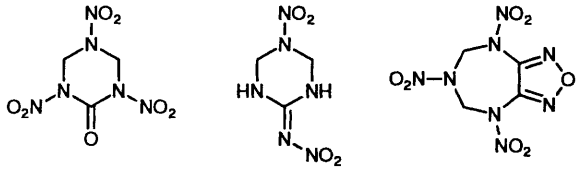
Secondary amines (diaryl, dialkyl, and aryl akyl) are converted into the corresponding nitramines by reaction with ethereal Grignard reagents (to give the corresponding RNR'MgBr), followed by treatment with $BuONO_2$ in benzene or hexane (**Scheme 16**).[41]



Scheme 16

The influence of the type of substituent on the ring nitrogen on the nitration of azetidines by dinitrogen pentoxide (N_2O_5) has been investigated and was found to play a critical role in determining the chemistry of the system.[42] Thus for N-alkyl or ethoxycarbonyl substituted derivatives, 1,3-nitramine-nitrate products are formed by a novel ring-opening nitration reaction analogous to that established for aziridines.[43] In contrast, azetidines bearing N-acyl substituents (acetyl, butyryl, or carbamyl) undergo preferential nitrolysis of the exocyclic substituent to form N-nitroazetidines whilst azetidines bearing strongly electron-withdrawing groups, such as picryl, are inert to attack by N_2O_5. The different reactivity of azetidines compared with aziridines can be rationalized in terms of the reduced ring strain of the four-membered ring series.

Cyclocondensation of urea, guanidine, or 3,4-diaminofurazan with formaldehyde and potassium sulfamate, followed by nitration, leads to the formation of the heterocyclic nitramines **10**, **11**, or **12** respectively.[44]



10 11 12

A molecular orbital study of the effects of electron correlation of the N–N bond of nitramines has revealed a considerable lengthening of both the N–NO_2 bond as compared to the N–NH_2 bond and

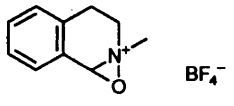
of C–C bonds, which can be attributed to the antibonding character of the N–NO_2 bond in the LUMO.[45] The results also suggest the importance of the N–NO_2 bond in the impact sensitivity of crystalline nitramines. The thermal decomposition of nitramines has been studied and found to show first-order reaction kinetics with the triggering mechanism believed to be homolysis of the N–NO_2 bond, in agreement with the above theoretical studies.[46]

5 Nitroso compounds

A review of the reactions of nitroso compounds has recently been published.[1]

The significant developments and changes in the chemistry and biochemistry of nitrosamines and other *N*-nitroso compounds over the last twelve years, with a particular emphasis on the implications of endogenous nitrosation in living cells, has been reviewed as part of the ACS Symposium Series.[47] The methods for analysis of *N*-nitroso compounds, with particular reference to human biomonitoring, have also been reviewed as part of the same series.[48]

The oxaziridinium tetrafluoroborate **13**, derived from dihydroisoquinoline, acts as an oxygen transfer reagent for the conversion of primary alkylamines into the corresponding nitroso compounds.[49] Anilines, however, are converted into nitro compounds and tertiary amines form *N*-oxides, whilst secondary amines and imines are converted into the corresponding nitrones.

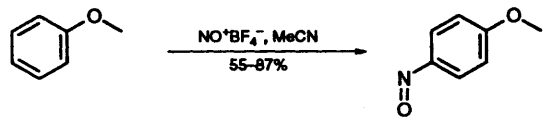


13

N-Alkyl and *N*-aryl indoles react with *N*-nitrosodiphenylamine, in the presence of catalytic amounts of trichloroacetic acid, to give the corresponding 3-nitroso derivatives in good yields.[50] In contrast, under identical conditions, *N*-H indoles (and *N*-OH indoles) give the corresponding 3-oximes (3-isonitroso compounds).

Direct nitrosations of aromatic hydrocarbons and anisoles are possible with the electrophilic nitrosonium cation NO^+, with $NO^+BF_4^-$ as the preferred nitrosonium salt (**Scheme 17**).[51] Reactions occur under mild conditions in which the more conventional procedure, based on nitrite neutralization with strong acid, is ineffective. The reactivity patterns for NO^+ aromatic nitrosations differ from previously established electrophilic aromatic nitrosation. This is ascribed to the rate-limiting deprotonation of the reversibly formed Wheland intermediate, which for aromatic nitration with NO_2^+ occurs with no deuterium isotope effect.

Transnitrosation by NO-carrying *O*-nitrosoisoureas, such as *N*-aryl-*N*-nitrosoureas allows the facile conversion of indolines, *N*-alkylanilines, and related compounds into their *N*-

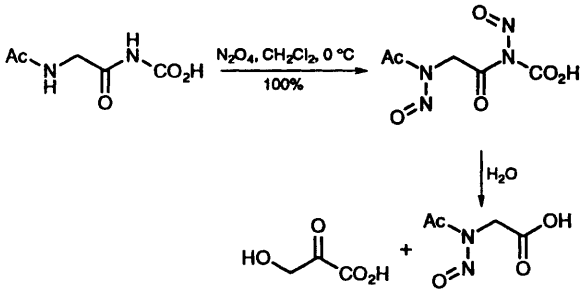


Scheme 17

nitroso derivatives.[52] The transnitrosation reactions are accelerated by electron-releasing groups on the acceptor molecules. The reaction is thought to proceed via thermal decomposition of the *N*-nitrosourea to form NO and a ureidyl radical, followed by formation of the NO-carrying agent, a *O*-nitrososiourea intermediate, and subsequent nitrosation of the substrate aniline or urea.

Many *C*-nitroso compounds form stable dimers containing a covalent N–N bond. A theoretical study of the reaction $2HNO \rightarrow (HNO)_2$ has been carried out to try to gain an insight into this dimerization process. Calculations for the reaction energy of formation of the *trans*-isomer have predicted a value of between -16.4 and -17.2 kcal mol^{-1} and an equilibrium constant for the association to the *trans*-dimer of $K_p = 259$ atm, indicating that the dimer should be observable in the gas-phase.[53]

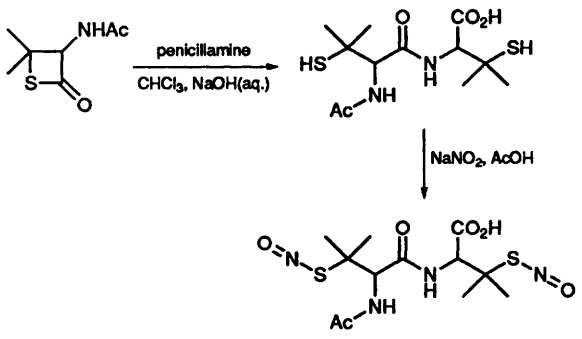
There has been significant recent interest in *N*-nitrosopeptides as potential carcinogenic agents, especially since *N*-nitrosopeptides can potentially arise naturally from *in vivo* reactions of the parent peptide. This emphasis has prompted an investigation of the nitrosation of amino acid and peptide derivatives. Thus, although the esters of *N*-protected α-amino acids and peptides readily yield stable *N*-nitroso products, the parent acids have been rather more elusive. However, *N*-acylamino acids and peptides are nitrosated readily by reaction with excess N_2O_4 in CH_2Cl_2, and the resulting *N*-acyl-*N*-nitrosoamino acids and peptides can be easily isolated (**Scheme 18**).[54] The resulting *N*-nitroso-acylamino acids and polynitrosoacylpeptides are readily hydrolyzed with cleavage occurring preferentially at the C-terminus.



Scheme 18

A range of novel *S*-nitroso analogues of penicillamine dipeptides has been prepared as potential slow-release agents for NO *in vivo*.[55] The optimum conditions for the preparation of a key compound in this area, *N*-acetyl-*S*-nitroso-penicillamine (SNAP), have been determined as sodium nitrite in an acidic media, such as AcOH.

This procedure is highly effective, in contrast to a range of alternative conditions. The similar nitrosations of penicillamine dipeptides under these conditions give the corresponding bis-thionitroso compounds (**Scheme 19**).



Scheme 19

The addition, reduction, and oxidation reactions of nitrosobenzenes have been reviewed, with a special emphasis on the reactions of nitrosobenzenes with nitrogen nucleophiles.[56]

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