DOI: 10.1070/RCR4662

Nitrosonium cation in chemical and biochemical reactions: achievements and prospects †

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Data on the reactivity of nitrosonium cation in chemical reactions are systematized and integrated. The review demonstrates the structural diversity of nitrosonium complexes resulting from the specific features of the electronic structure of NO^+. The use of nitrosonium salts in the synthesis of heterocyclic compounds and for the preparation of modern materials, including nanomaterials, is considered. The participation of NO^+ in oxidative, catalytic and biochemical processes is discussed. The bibliography includes 332 references.

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I. Introduction

A nitrosonium cation is a reactive intermediate in numerous chemical and biochemical reactions. The NO^+ cation is pertinent to the chemistry of the ionosphere[1] and has a direct or indirect effect on ozone layer depletion in the Earth's stratosphere.[2,3] The reaction of this cation with atmospheric water vapour gives nitrous acid (HNO_2), the extent to which NO^+ and water interact being determined by the geometry of $NO^+ \cdot n\,H_2O$ clusters.[4] The chemistry of the NO^+ ion is essential for the understanding of the biological role of nitrogen(II) oxide.[5,6] The elucidation of the detailed mechanism of DNA damage by NO^+ is of vital importance to the understanding of the modification of genetic material and evolution of living organisms.[7] In chemical reactions, the NO^+ cation is generated by treating metal nitrites in water or mixed solvents ($AlkOH - H_2O$) or nitrite ionic liquids with strong acids, as well as using directly nitrosonium salts with different anions (BF_4^-, PF_6^- and so on).[8–10] The following compounds can serve as sources of the nitrosonium cation: HNO_2, NOCl, N_2O_3, N_2O_4, Fremy's salt $[(KO_3S)_2NO]$, $[NO^+ \cdot \text{crown} \cdot H(NO_3)_2^-]$ complexes, $Na_2N_2O_3$, bis(triphenylphosphine)nitrogen(1+) nitrite, alkyl nitrites, nitrite ionic liquids.[8–11] The nitrosonium cation is a strong oxidizer, which is often employed in oxidation reactions of different classes of organic compounds.[12] Nitrosonium salts are widely used for the preparation of heterocyclic compounds and nanomaterials. The NO^+ cation is a key intermediate in nitrosation and diazotization reactions; it forms complexes with many organic compounds.[13] Nitrosonium complexes have been a subject of keen interest for many years because they serve as intermediates in a number of important organic reactions, such as nitrosation of aromatic compounds and nitrosohalogenation of alkenes, and are evidently involved in biochemical processes.[13–16] This interest has grown after

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Current research interests: theoretical and applied aspects of fine organic synthesis, cationic complexes of organic compounds, organic reactions in ordered media.

Received 27 April 2016
Translation: T.N.Safonova

† Dedicated to the memory of Academician V.A.Koptyug.

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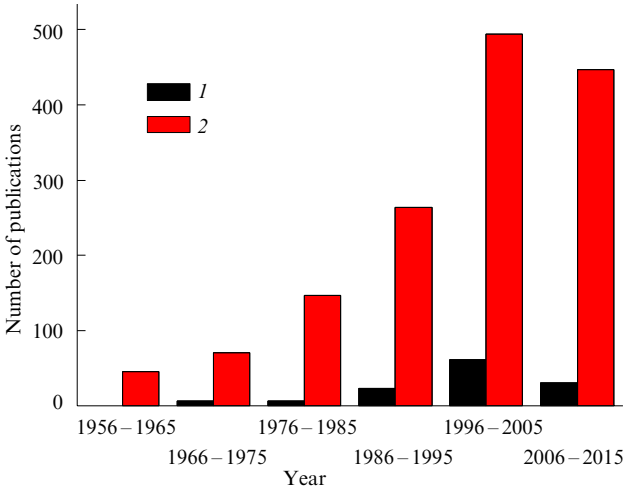


Figure 1. Cited references including the keyword 'nitrosonium' found with SciFinder.
(*1*) Patents, (*2*), all references.

the discovery of the unique role of the NO molecule in fine biochemical processes taking place *in vivo*.[17–19] It is assumed that the NO^+ cation and some molecules serving as a source of this cation are involved in the mechanisms of neurodestructive, neuroprotective and antitoxic effects of nitric oxide[13,20] and are likely to be participants in the reaction resulting in DNA cross-linking.[21–23]

The growing interest in the chemistry of the nitrosonium cation can be seen from the cited references searched with SciFinder including the keyword 'nitrosonium' (Fig. 1). A Web of Science search performed for articles including this keyword gave 2300 references over the last 10 years.

The goal of the present review is to systematize and analyze the data published in the last 10–15 years on the involvement of the nitrosonium cation in chemical and biochemical processes. Earlier publications are referred to only if they are required for an understanding of the essence of the issue and consideration of new trends in the area of interest.

II. Nitrosonium complexes of organic compounds

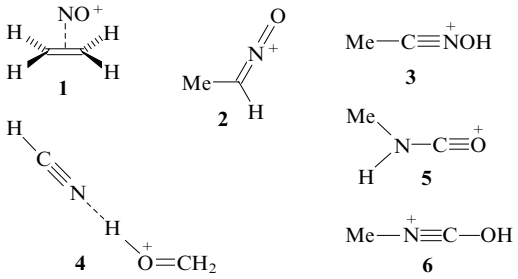
II.1. Alkene complexes

The ionization potential of the NO molecule (9.264 eV)[1] is similar to those of some unsaturated organic molecules. Therefore, the nitrosonium cation can form charge-transfer (CT) complexes with these compounds. Nitrosonium complexes of alkenes and aromatic compounds are considered in sufficient detail in the review[24] published in 2001. Here, we will analyze more recent data.

Gerbaux *et al.*[25] calculated the potential energy surface for the ethylene complex with NO^+ by quantum chemical methods at the G2 and G3B3 levels of theory. They found 19 local structures. The global energy minimum, which is $\sim 65\ kJ \cdot mol^{-1}$ lower in energy with respect to the starting ethylene + NO^+ system, corresponds to structure **1**.

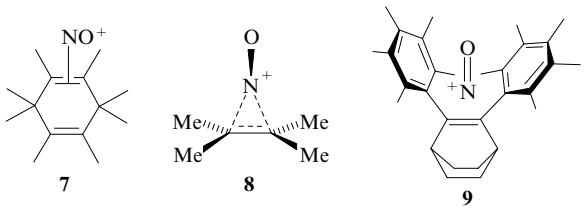
The formation of complex **1** was confirmed by mass spectrometry in experiments on collisions of $H_2O \cdot NO^+$ with ethylene. Complexes **2**–**6** correspond to local minima and are kinetically stable with respect to isomerization and dissociation.

Structures 1–6



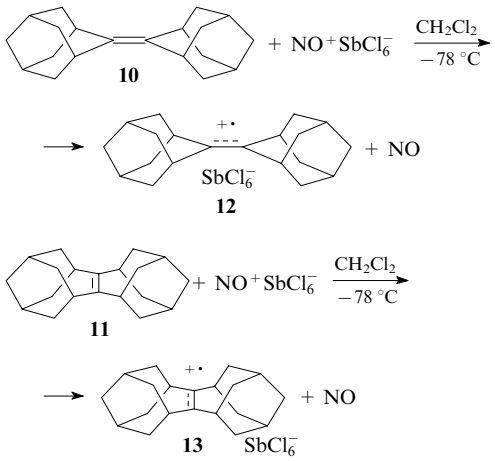
Reliable experimental data on the formation of alkene–NO^+ complexes in solution are scarce. First data were reported for the 1,2,3,3,4,5,6,6-octamethyl-1,4-cyclohexadiene complex with the NO^+ cation (**7**).[26] Later on, the nitrosonium complex of 2,3-dimethylbut-2-ene was prepared (**8**).[27] According to the X-ray diffraction data, the reaction of the nitrosonium cation with 1,2-bis(pentamethylphenyl)bicyclo[2.2.2]oct-2-ene gives complex **9**, in which the double bond is apparently weakly involved in the interaction with the NO group.[28]

Structures 7–9



In reactions with unsaturated compounds, the nitrosonium cation usually acts as an electrophilic agent. However, NO^+ serves as an oxidizer in reactions with sterically hindered alkenes to form radical cations. Rathore *et al.*[29] demonstrated that adamantylideneadamantane (**10**) and sesquihomoadamantene (**11**) react with the $NO^+SbCl_6^-$ salt in CH_2Cl_2 at low temperatures under an inert atmosphere (Ar) and produce radical cations **12** and **13**, respectively, rather than π-complexes (Scheme 1).

Scheme 1



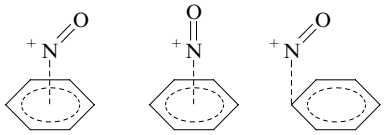
The reaction of adamantylideneadamantane in the presence of oxygen yields the corresponding epoxide.

II.2. Nitrosonium complexes with aromatic compounds

Complexes of the nitrosonium cation with mono- and polycyclic aromatic compounds were studied rather extensively. These complexes have attracted the attention of organic chemists due primarily to the fact that they are analogues of intermediates in such important reactions as diazotization, C-nitrosation and nitration of aromatic compounds through intermediate nitrosation.[13,24]

A comparison of the data obtained by multiphoton dissociation spectroscopy and the IR frequencies calculated at the B3LYP/6-311+G** level of theory for gas-phase structures **14a**,**b** and **15**, which are generated by the reaction of benzene with NO^+, demonstrated that complex **14a** is the most stable one.[30]

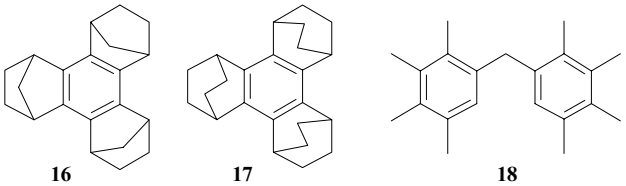
Structures 14, 15



14a **14b** **15**

According to the results of calculations at the CCSD(T)/6-31G** level of theory, the reaction of the NO^+ cation with benzene in the gas phase affords a π-complex rather than a σ-complex that is produced in reactions with nitronium cations.[31] Calculations of the energy profiles corresponding to the [$PhHNO^+$] and [$PhH^{+\bullet} + {}^{\bullet}NO$] systems, respectively, as a function of the distance between the N atom and the centre of the benzene ring with fixed C_{2v} symmetry demonstrated that the radical pair is not involved in the nitrosation of benzene.[32] Substantial differences in the interaction of NO^+ and NO_2^+ cations with benzene were revealed[33] in terms of the valence bond theory. For the NO_2^+ cation to form π-complexes, a rather high energy is required to deform the O=N=O moiety, the extent of electron density transfer from the benzene ring to this cation being much greater compared to NO^+. The formation of a σ-complex is more favourable for the NO_2^+ cation than for NO^+. In the case of the NO^+ cation, the transition from the π-to σ-complex has a higher barrier compared to NO_2^+. The mass-spectrometric study demonstrated that the reaction of protonated monosubstituted benzenes PhX (X = H, CN, CHO, CO_2Me, Ac, NO_2) with Bu^tONO in the gas phase produces stable nitrosonium complexes.[34] According to calculations at the B3LYP/6-311++G(d,p) level, the π-complex is most stable for benzene, while the n-complex is most stable for pyridine.[34] The formation of nitrosonium complexes of durene, pentamethyl- and hexamethylbenzenes in the reaction of CF_3CO_2H with n-octyl nitrite in CH_2Cl_2 in the presence of aromatic donors was confirmed by IR and electronic absorption spectroscopy (EAS).[35] The hexamethoxybenzene–NO^+ charge-transfer complex was studied by laser-induced fluorescence and femtosecond transient absorption spectroscopy.[36] A solution of this complex in MeCN showed weak fluorescence with a spectrum similar to that observed for the excited hexamethoxybenzene (HMB) radical cation. Short-lived states (6.6 ps) corresponding to a low fluorescence quantum yield (2.5×10^{-5}) were detected by femtosecond laser flash photolysis, which allowed the assignment of these states to the [$HMB^{+\bullet}$*/$NO^{\bullet}$] pair. Nitrosonium complexes of benzene and analogues of aromatic amino acids (phenylalanine, tyrosine, histidine and tryptophan), in which the $CH_2CH(NH_2)CO_2H$ moiety is replaced by the CH_3 group, were studied by the B3LYP and MP2 methods.[37] At all levels of theory, these complexes are similar to the nitrosonium complex of benzene, the NO group being located closer to the alkyl moiety. Apart from the [$ArH\cdot NO^+$] structures, sandwich-type structures [$ArH\cdot NO^+\cdot ArH$] were found. For the histidine analogues, the n-complex, in which the NO group is bound to the endocyclic N(1) atom, proved to be energetically most favourable. The formation of coloured [$ArH\cdot NO^+$] complexes (1 : 1) [ArH is benzene, toluene, *o*-xylene, *p*-xylene, mesitylene, 1,3,5-tris(*tert*-butyl)benzene, durene, 1,2,4,5-tetraisopropylbenzene, pentamethylbenzene, pentaethylbenzene, hexamethylbenzene, hexaethylbenzene, bi- and polycyclic hydrocarbons **16**–**18**] is accompanied by the appearance of a long-wavelength charge-transfer band (425–553 nm) in the electronic absorption spectrum.[38]

Structures 16–18

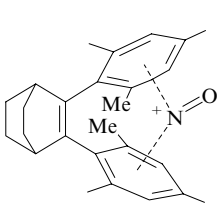


16 **17** **18**

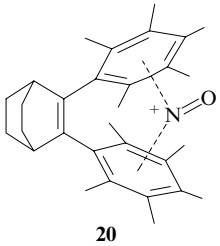
The results of IR spectroscopy and X-ray diffraction are indicative of the outer-sphere character of the resulting complexes, with the distance between the nitrogen atom of the NO^+ cation and the aromatic ring being much smaller (2.0–2.2 Å) than the sum of the van der Waals radii of the carbon and nitrogen atoms (3.25 Å). There is a linear relationship between logarithms of formation constants for $ArH\cdot NO^+$ complexes in CH_2Cl_2 ($\log K_{CT}$) and the oxidation potentials (E°_{ox}) of aromatic compounds. The intermolecular electron transfer between the aromatic donor and NO^+ occurs with the participation of [ArH, NO^+] complexes followed by the formation of a radical cation and nitrogen oxide [$ArH^{+\bullet} + NO^{\bullet}$].[39] The structure optimization of nitrosonium complexes of substituted benzenes containing CHO, Ac, Bz, CN, NO or NO_2 substituents in the benzene ring at the DFT/PBE/3z and RI-MP2/L1 levels of theory gave n- rather than π-complexes.[40] In the series of nitrosonium π-complexes of PhX (X = Me, Et, Pr^n, Pr^i, Bu^t, F, Cl, CF_3), the complexes with a η^2- or η^3-coordination mode are energetically more favourable, the geometric parameters being similar to those determined for hexamethylbenzene and other arenes by X-ray diffraction.[24,38] Both the calculations and experimental data showed that the common features of these complexes are the angular arrangement of the NO group with respect to the benzene ring plane, the sp^2-hybridization of carbon atoms of the aromatic ring and large distances between the nitrogen atom of the NO group and the nearest carbon atoms of this ring (~2 Å). The angular arrangement of the NO group with respect to the aromatic ring is also characteristic of π-complexes **19**–**24** with polycyclic compounds.[41]

According to the results of calculations at the DFT/PBE/3z level of theory, the formation of chelate complexes **19** and **20**, in which the NO^+ cation is bound to two aromatic rings, is energetically more favourable than the formation of complexes, in which this cation is present in the outer sphere and is bound to one of the aromatic rings. There are linear relationships[41] between the affinities of

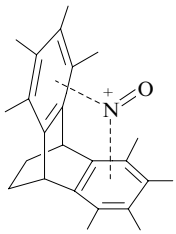
Structures 19–24



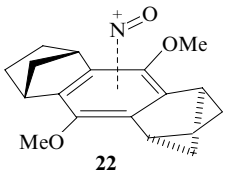
19



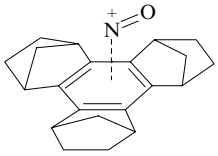
20



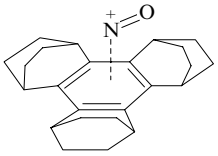
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22



23

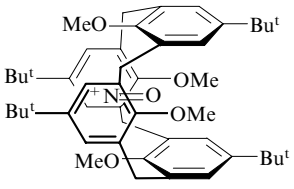


24

aromatic compounds for the nitrosonium cation calculated at the DFT/PBE/3z and RI-MP2/L1 levels of theory and the values of $\log K_p$ (K_p is the formation constant of the complex with NO^+) in CH_2Cl_2 and MeCN.[38,42–45]

In π-complexes of aromatic compounds, including 2 : 1 bis-arene nitrosonium complexes, the NO group is usually inclined to the plane of the aromatic ring.[24,38,46] As opposed to these complexes, calixarene captures the nitrosonium cation in such a way that the latter is nearly parallel to the aromatic rings,[41] resulting in the formation of very stable complex **25** ($K_p > 10^8$ litre mol^{-1} in CH_2Cl_2).[47]

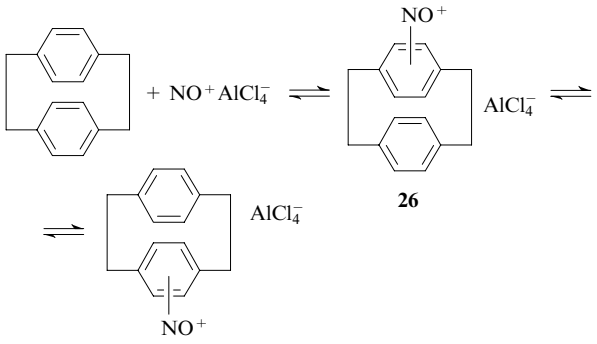
Structure 25



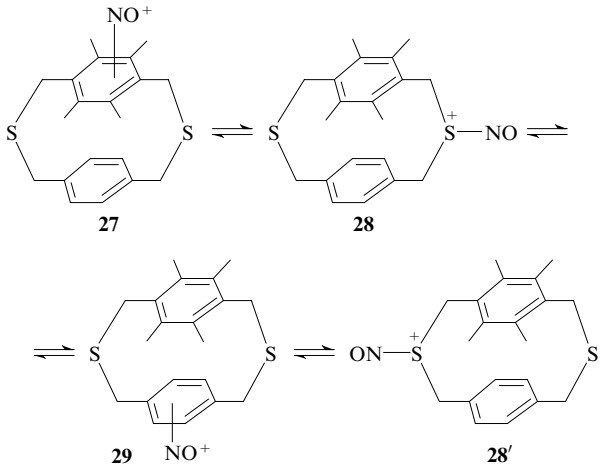
25

Enhanced stability of nitrosonium complexes of calixarenes was proposed to employ for fixation of N_xO_y gases.[48–59] Calixarene-based nanotubes can also be used for fixation of nitrogen oxides, resulting in the formation of nitrosonium complexes.[60–62] Apart from nitrogen oxides, NO^+X^- salts[47] and alkyl nitrites[63] can interact with calixarenes, thus serving as a source of nitrosonium cations. Calixarene tubes encapsulating five NO^+ cations were synthesized.[64] The reactions of resorcin[4]arenes with $NO^+BF_4^-$ produce quite stable 1 : 1 and 1 : 2 nitrosonium complexes that entrap a precursor of the nitrosonium cation within their cavities.[65,66] As opposed to these complexes, the cavity sizes of paracyclophane and 5,6,8,9-tetramethyl-2,11-dithia[32](1,4)cyclophane are too small to encapsulate NO^+ within the inner cavity of these molecules, resulting in the formation of outer-sphere dynamic complexes **26**, **26′** and **27–29**, respectively (Schemes 2 and 3).[67,68]

Scheme 2

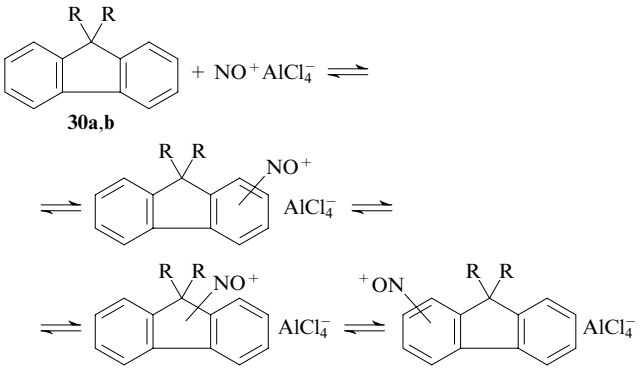


Scheme 3



Dynamic nitrosonium complexes were also detected by ^1H and ^{13}C NMR spectroscopy for fluorene (**30a**), 9,9-dimethylfluorene (**30b**) and triptycene (**31**) (Schemes 4 and 5).[69,70]

Scheme 4

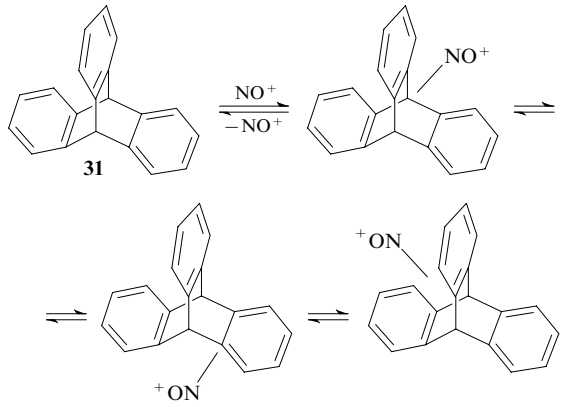


R = H (**a**), Me (**b**)

Rearrangements of these complexes are not frozen on the NMR time scale even at < -70 °C.

The totality of the calculated and experimental data provide evidence that reactions of the nitrosonium cation with aromatic compounds usually afford π-complexes

Scheme 5



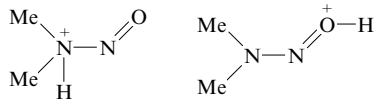
rather than σ-complexes. For heterocyclic and aromatic compounds containing C(O)R (R = H, Me, Ph), CN, NO and NO_2 substituents, n-complexes are energetically more favourable.

II.3. Nitrogen-centred nitrosonium complexes

Nitrosonium complexes with amines and N-heterocyclic compounds were assumed as intermediates in diazotization, nitrosation of amides and N-heterocyclic compounds, the formation and denitrosation of nitrosamines, *etc.*[13, 71–74]

Sun *et al.*[75] studied the formation of *N*-nitrosodimethylamine by nitrosation of trimethylamine at the CBS-QB3 level of theory. Initially, the reaction produces the nitrosonium complex of trimethylamine Me_3N^+-NO, which is transformed into the iminium cation $Me_2N^+=CH_2$. In the Me_3N^+-NO complex, the N–N bond is rather long (1.884 Å); the N–N–O angle is 111.9°. The protonation of *N*-nitrosodimethylamine in the gas phase was studied by ion cyclotron resonance.[76] It is assumed that, in the presence of Bu^nONO, the reaction produces the NO^+ cation, which is attached to the nitrogen atom of Me_2NH to form nitrosonium complex **32a**, and the latter is transformed into more stable complex **32b**.

Structures 32



32a **32b**

An unusual complex of phenanthroline with $NO^+BF_4^-$ was detected by ^1H and ^{13}C NMR spectroscopy and X-ray diffraction.[77, 78] In this complex, the NO group is located between two nitrogen atoms. Therefore, this complex should be assigned to bidentate complexes (Fig. 2). The crystal structure contains two types of cations characterized by the N^1-N bond lengths of 2.250 and 2.338 Å and the $N^{10}-N$ bond lengths of 2.284 and 2.344 Å. These values are smaller than the sum of the van der Waals radii of two nitrogen atoms (3.0 Å). The N–O group is inclined at an angle of 54° and 61° to the plane of the phenanthroline core. The geometric parameters calculated at the HF/6-31G level are similar to the experimental values.

The reaction of $NO^+BF_4^-$ with *para*-substituted *meso*-tetraarylporphyrins **33a–e** at room temperature gives 1 : 1 nitrosonium complexes.[79] Based on the results of ^1H and ^{13}C NMR, IR and UV spectroscopy, the authors suggested that the porphyrin macrocycle is non-planar and the NO^+

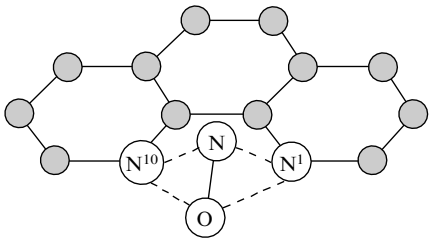
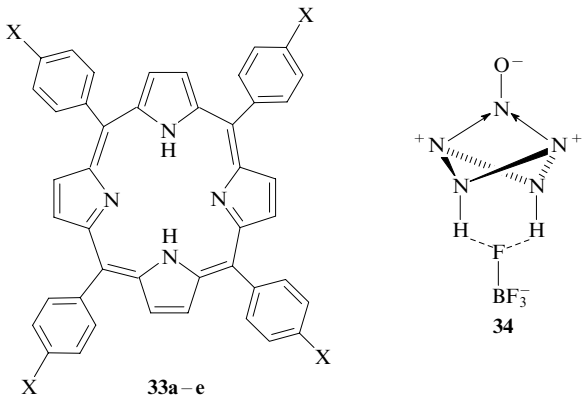


Figure 2. X-Ray structure of the nitrosonium complex of phenanthroline.[78]

cation in the complex is bound to two nitrogen atoms, the NO group being on one side of the macrocycle, whereas two pyrrole H atoms being on the other side (Structure **34**).

Structures 33, 34



33a–e **34**

X = H (**a**), Me (**b**), Pr^i (**c**), OMe (**d**), Cl (**e**)

The ^1H NMR spectrum of porphyrin complex **33a** shows a signal of NH groups in an extraordinarily high field ($\delta = -2.80$ ppm). This fact was attributed to the formation of weak hydrogen bonds with the fluorine atom of the BF_4^- anion (see Structure **34**). An extensive series of mono- (**35**) and disubstituted (**36**) pyridines, pyridazine, pyrimidine, pyrazine, 1,3,5-triazine, quinoline, isoquinoline, cinnoline, quinoxaline, acridine, phenazine and bicyclic

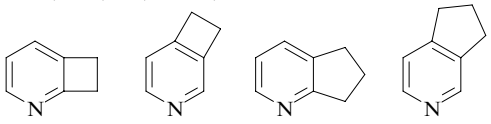
Structures 35–40



35 **36**

X = 2-Me, 2-Et, 2-CF_3, 2-CN, 2-OMe, 2-SMe, 2-Br, 2-Cl, 2-F, 2-NH_2, 3-Me, 3-CF_3, 3-Ac, 3-Bz, 3-OH, 3-OMe, 3-SMe, 3-Br, 3-Cl, 3-F, 3-NH_2, 4-Me, 4-Et, 4-CH=CH_2, 4-Ph, 4-CF_3, 4-OMe, 4-SMe, 4-Br, 4-Cl, 4-F, 4-NH_2, 4-NO_2

X = 2-Me: Y = 3-Me, 4-Me, 5-Me, 6-Me;
X = 3-Me: Y = 4-Me, 5-Me;
X = 2-Cl: Y = 4-Me, 6-Me, 6-OMe



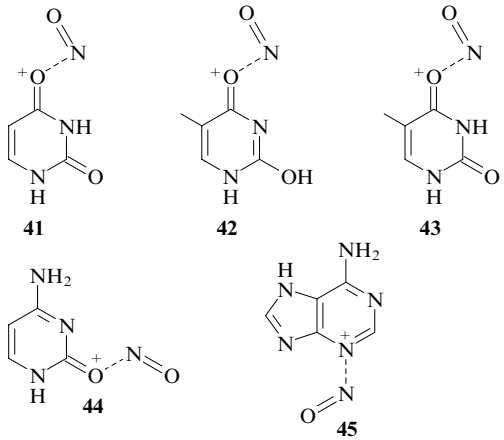
37 **38** **39** **40**

pyridine derivatives **37**–**40** were studied by quantum chemical methods at the HF and MP2 levels of theory.[80]

Qualitatively similar patterns were obtained by analyzing the influence of the structural factors on the affinity for the nitrosonium cation (A_{NO}^{+}) by means of different quantum chemical methods [HF/6-31G, HF/6-31G(d), HF/6-31G+(d), HF/6-31G(2d), HF/6-31G(d,p), HF/6-31G(2d,p), MP2/6-31G]. For substituted pyridines, the A_{NO}^{+} value increases with an increase in the electron-donating character of substituents. In accordance with the theory of resonance, the $+M$ effect is most pronounced for substituents at positions 2, 4 and 6. An increase in the number of nitrogen atoms in the azine ring leads to a decrease in the affinity for nitrosonium. There is a linear correlation between the calculated A_{NO}^{+} values and the experimental proton affinities (PA), which, taking into account the availability of the latter, can serve as the basis for the estimation of unknown values of $A_{NO}+$.

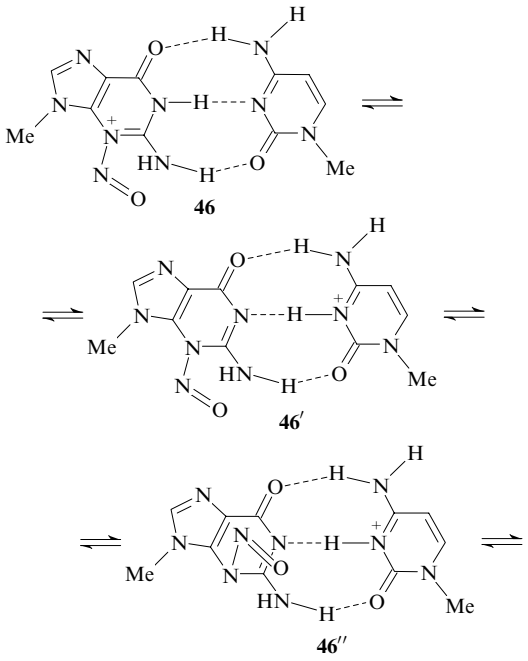
Nitrosonium complexes of uracil, thymine,[81] cytosine[82] and adenine[83] were studied by the RI-MP2/L1 method. It was found that n-complexes **41**–**45**, in which the NO^{+} cation is coordinated to oxygen or nitrogen atoms, is energetically most favourable for different tautomeric forms of these bases. The experimental affinity of the diketo form of thymine for nitrosonium is in agreement with the calculated value. There is a linear relationship between the A_{NO}^{+} values for tautomeric forms of uracil and thymine having similar geometric parameters. Nitrosonium complexes of 1-methylcytosine and 9-methylguanine, which are structural analogues of the nucleotide bases cytosine and guanine, as well as of their complementary pair, were studied by the RI-MP2/L1 method.[84] The addition of the nitrosonium cation to these compounds and their pair gives a series of nitrosonium complexes of different types ($\eta^1-\eta^3$). n-Complexes, in which the NO^{+} cation is coordinated to nitrogen and oxygen atoms, are usually energetically more favourable than π-complexes. The complex, in which the NO^{+} cation is coordinated to the carbonyl oxygen atom and the N(7) atom of the guanine moiety of the pair, is characterized by the global minimum on the potential energy surface. The interactions of nitrosonium complexes of 1-methylcytosine and 9-methylguanine with 9-methylguanine and 1-methylcytosine, respectively, are energetically more favourable than the interactions giving the neutral 1-methylcytosine–9-methylguanine pair. Some nitrosonium complexes of the pair are of dynamic nature. For instance, the rearrangement of complex **46** through intermediate complex **46′** into complex **46″** has a very low activation energy (11.6 kJ mol^{-1}). The first step involves the hydrogen migration from position 1 of the guanine moiety to position 3 of cytosine accompanied by the alteration of charges of the components in the nitrosonium complex (Structure **46′**). This is followed by the through-space migration of the NO group to form π-complex **46″** (n,π-rearrangement) (Scheme 6).

Structures 41–45



41 **42** **43** **44** **45**

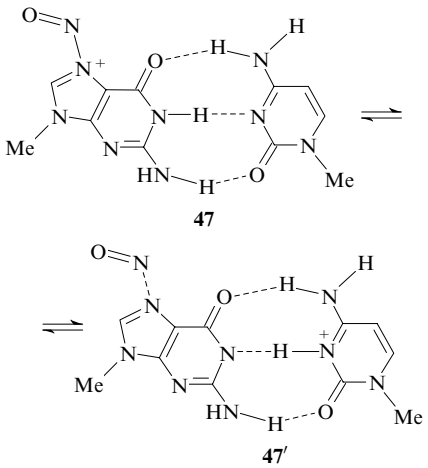
Scheme 6



46 **46′** **46″**

The rearrangement accompanied by hydrogen transfer from the guanine moiety to cytosine was observed also for complex **47**, which is transformed into complex **47′** (Scheme 7).

Scheme 7



47 **47′**

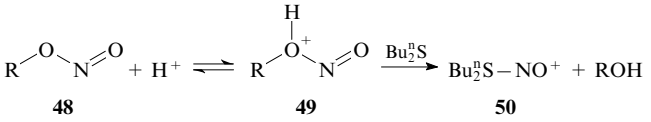
The energy barriers for the forward and backward reactions are 26.7 and 3 kJ mol^{-1}, respectively. Similar low-energy barrier rearrangements were found by the RI-MP2/L1 method for nitrosonium complexes of the 9-methyladenine–1-methylthymine complementary pair.[85]

II.4 O,S-Centred nitrosonium complexes

Complexes of the nitrosonium cation with compounds containing Group VI atoms were assumed as intermediates in many reactions, for example, in reactions with O-bases (alcohols,[86] ketones[87]), S-bases (desulfurative fluorination of thioesters,[88] transformation of thioketones and thioamides into ketones and acid amides, respectively[89]) and some other processes.[90,91] As mentioned above, $NO^+ \cdot (H_2O)_n$ clusters play an essential role in atmospheric processes,[2–4] and the extent to which the NO^+ cation and water form nitrous acid substantially depends on the geometric arrangement of the water molecules in the cluster.[4]

The mechanism of the intracluster reaction of the NO^+ cation surrounded by four and five water molecules, resulting in the formation of an HONO molecule, was studied at the MP2/aug-cc-pVTZ level of theory.[92] New structures of isomers of $NO^+ \cdot (H_2O)_n$ clusters ($n = 4$ and 5) and transition states for this reaction that proceeds with low barriers (17.1 and 14.2 kJ mol^{-1}, respectively) were found. These data are consistent with the above-mentioned short lifetime of NO^+ in water. According to the *ab initio* calculations (at the G3 and CBS-Q levels), the acid H_2ONO^+ is stronger than HONO.[93] The affinities for the nitrosonium cation calculated at the G2(MP2) level for ROH, RSH and RNH_2 molecules (R = H, Me) are quite similar to the experimental values.[94] The A^+_{NO} values for S-bases are higher than those for O-bases. The distances between the nitrogen atom of the NO group and the O and S atoms in $R^1R^2O-NO^+$ $R^1R^2S-NO^+$ complexes (R^1, R^2 = H, Me) are 2.0–2.2 and 2.3–2.5 Å, respectively, being smaller than the sum of the van der Waals radii of the N···O and N···S atoms.[94] The reaction of n-octyl nitrite (**48**) with trifluoroacetic acid gives O-centred complex **49**, and the treatment of the latter with Bu^n_2S produces the $Bu^n_2S-NO^+$ complex (**50**) (Scheme 8).[35]

Scheme 8



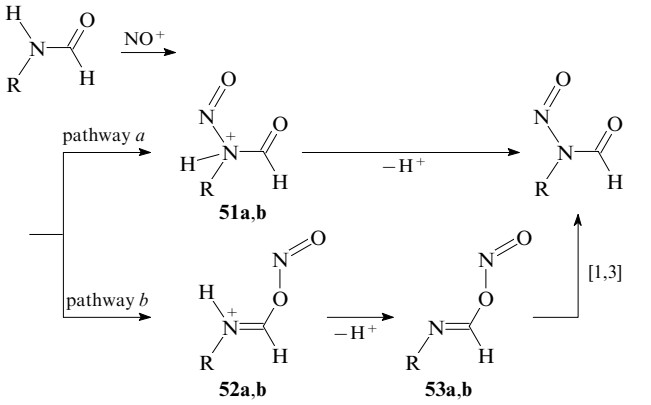
48 **49** **50**

R = n-C_8H_{17}

The enthalpy of formation of nitrosonium oxalate $(NO^+)_2[O_2CCO_2]^{2-}$ was calculated at the CBS-4M level of theory.[95] In the gas phase, the ionic form $(NO^+)_2[O_2CCO_2]^{2-}$ is less stable than the covalent structure $ON-O_2C-CO_2-NO$. The pathways of nitrosation of formamide and *N*-methylformamide with nitrosonium cations were investigated at the B3LYP/6-31G(d,p) level of theory.[96] Two mechanisms of the reaction giving complexes **51a**,**b** and **52a**,**b** were considered. The key step of the transformation *via* the pathway *b* is the low-energy barrier 1,3-sigmatropic shift of the NO group in structures **53a**,**b** (the activation barrier is 27.6 and 20.1 kJ mol^{-1}, respectively) (Scheme 9).

The kinetics of the reaction of esters AlkOCHO, AlkOC(O)Me, AlkOC(O)Pr^n and AlkOC(O)Bu^n with NO^+ was studied by selected ion flow tube mass spectrometry.[97] According to the CBS-4M calculations, the association of NO^+ at the carbonyl oxygen atom is more favourable than at the alkoxy oxygen atom. For example, the binding of the NO^+ cation to the carbonyl oxygen atom of *tert*-butyl propionate is 79.9 kJ mol^{-1} more favourable

Scheme 9



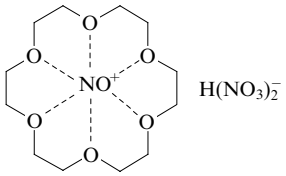
51a,**b** **52a**,**b** **53a**,**b**

R = H (**a**), Me (**b**)

in energy than the binding to the oxygen atom of the alkoxy group. The energy barrier for 1,3-migration of the NO group from the carbonyl to ester oxygen atom is very high and the rearrangement does not occur.

The reaction of $NO_2 \cdot N_2O_4$ with 18-crown-6 in CH_2Cl_2 at −10 °C gave nitrosonium complex **54**, which was used for the nitrosation of secondary amines.[98]

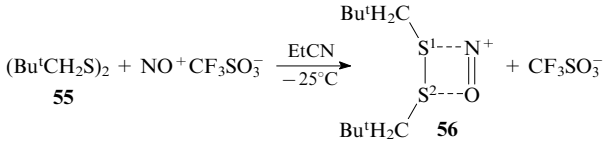
Structure 54



54

The reaction of nitrosonium triflate with di(neopentyl) disulfide (**55**) in EtCN produces unusual complex **56** with a four-membered ring (Scheme 10).[99] The S^1-N and S^2-O bond lengths determined by X-ray diffraction are 2.3035(7) and 2.8592(7) Å, respectively.

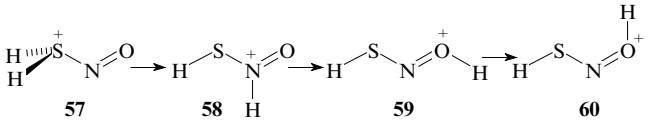
Scheme 10



55 **56**

The relative stability of isomeric nitrosonium complexes with H_2S was evaluated and the IR frequencies of these complexes were calculated at the CCSD(T)/aug-cc-pvtz level of theory.[1] Cation **57** is most stable in the series of isomeric ions **57**–**60** corresponding to hydrogen transfer (Scheme 11).

Scheme 11



57 **58** **59** **60**

ΔE /kJ mol^{-1}	0	43.9	35.1	67.7

The geometry and relative energies of nitrosonium complexes of thioacetamide and thiourea were calculated at the B3LYP/6-31+G(d,p) level of theory.[100] In the series of isomeric structures, *anti-trans*-ONSCMeCNH$_2^+$ and *anti*-ONSC(NH$_2$)$_2^+$ proved to be the most stable structures. According to the CBS-QB3 calculations in the gas phase, the nitrosonium cation can bind to *cis*- or *trans*-S-nitrosomethanethiol both at the nitrogen and sulfur atom to form nitrosonium complexes, the binding being an exothermic process that proceeds without an activation barrier.[101]

III. Nitrosonium cation as an oxidizer and catalyst in organic chemistry

The nitrosonium cation belongs to strong oxidizers ($E^\circ = 1.51$ eV) and oxidizes many organic compounds with the potential $E^\circ < 1.7$ eV;[12] it can also act as the catalyst for many chemical reactions.

III.1. Reactions of alkanes, alkenes, alkynes and their derivatives with the NO^+ cation

The use of zeolite catalysts holds promise in the selective catalytic reduction of nitrogen oxides with hydrocarbons. These investigations are important for environmental protection taking into account the wide application of motor fuels, combustion of which releases NO_x gases. The NO^+ cation is assumed to be involved in reduction of these gases with alkanes on H-ZSM-5 zeolite or mordenite.[102–104] The reaction rate of hydride transfer from alkane C_nH_{2n+2} to NO^+ changes only slightly at $n = 4–7$ but substantially increases at $n = 8–10$.[105] This reaction probably involves alkane oxidation as the first step (see, for example, Ref. 106). Branched C_7 and C_8 alkanes react in the gas phase with NO^+ to give $C_4H_{10}NO^+$, which undergoes dissociation through elimination of HNO.[106] It is believed that the reduction of an NO molecule with acetylene on mordenite or H-ferrierite catalysts proceeds with the participation of the nitrosonium cation.[107, 108] The formation of NO^+ was observed by Fourier-transform IR spectroscopy when studying the reduction of NO with alkanes on zeolites at high temperatures.[109] The nitrosonium cation reacts with haloalkanes to produce cations. The rate of the reaction of methyl iodide (**61**) in the gas phase depends on the number of NO^+ cations involved in the reaction [$n = 1–4$, $k \times 10^{10}$ (cm^3 s^{-1}) = 2, 9, 13 and 14] (Scheme 12).[110]

Scheme 12

$$CH_3I + NO^+ \longrightarrow CH_3I^+ + NO$$

61

A method was developed for the synthesis of methanol from methane based on the involvement of $NO^+HSO_4^-$ in the chemical process (Scheme 13).[111]

Scheme 13

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$

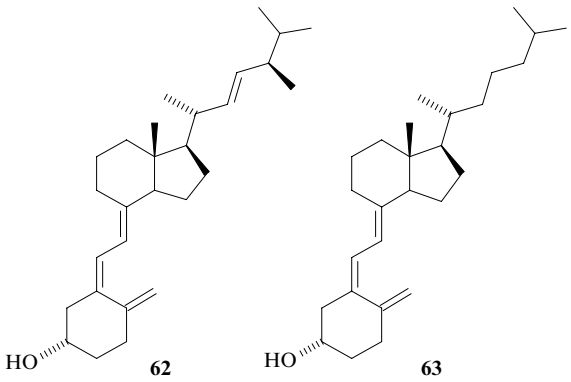
$$CH_3Cl + NO^+HSO_4^- \longrightarrow CH_3HSO_4 + NOCl$$

$$NOCl + H_2SO_4 \longrightarrow NO^+HSO_4^- + HCl$$

$$CH_3HSO_4 + H_2O \longrightarrow CH_3OH + H_2SO_4$$

The $NO^+SbF_6^-$ salt was used as a one-electron oxidizing agent for unsaturated natural compounds — vitamins D_2 (**62**) and D_3 (**63**).[112] As shown by NMR spectroscopy, the oxidation products do not contain a triene moiety.

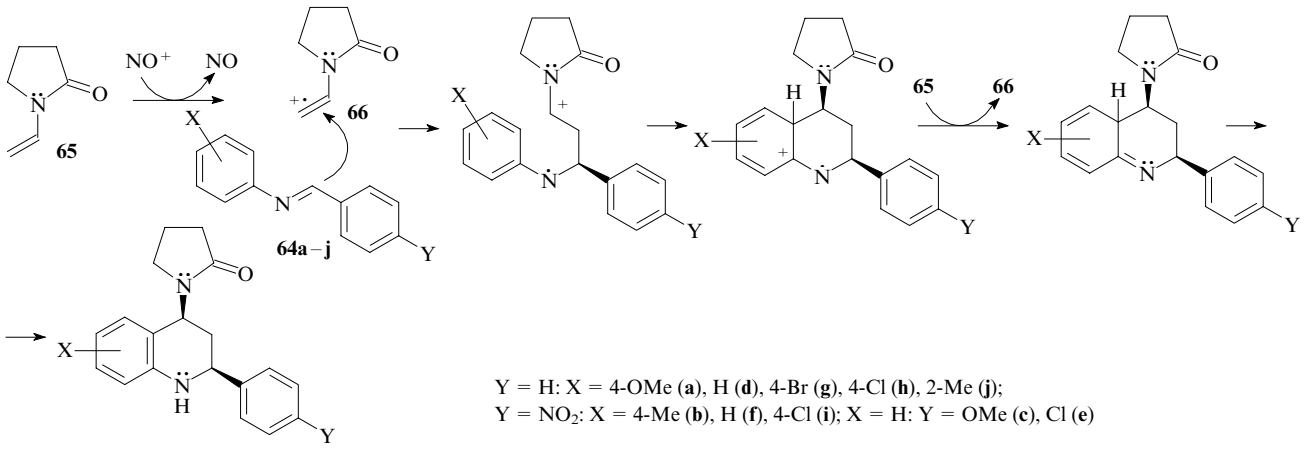
Structures 62, 63



62 **63**

The nitrosonium cation initiates the aza-Diels–Alder reaction of *N*-arylamines **64a–j** with *N*-vinylpyrrolidine (**65**) through its oxidation to radical cation **66** (Scheme 14).[113] The employment of the nitrosonium cation as an oxidizing agent in the aza-Diels–Alder reaction of *N*-arylamines with 2,3-dihydrofuran or 3,4-dihydro-2*H*-pyran allows the synthesis of furano[3,2-*c*]- or pyrano[3,2-*c*]quinolines in 24%–96% yields.[114]

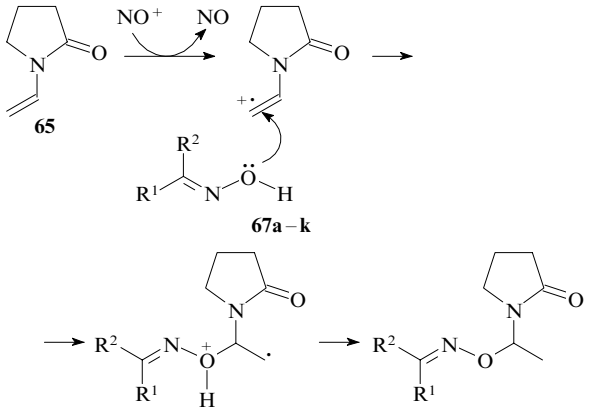
Scheme 14



Y = H: X = 4-OMe (**a**), H (**d**), 4-Br (**g**), 4-Cl (**h**), 2-Me (**j**);
Y = NO_2: X = 4-Me (**b**), H (**f**), 4-Cl (**i**); X = H: Y = OMe (**c**), Cl (**e**)

Wu *et al.*[115] studied the O-alkylation of oximes **67a–k** with *N*-vinylpyrrolidone (**65**) in the presence of nitrosonium tetrafluoroborate as the catalyst. The proposed reaction mechanism involves the oxidation of *N*-vinylpyrrolidone with NO^+ to the corresponding radical cation (Scheme 15).

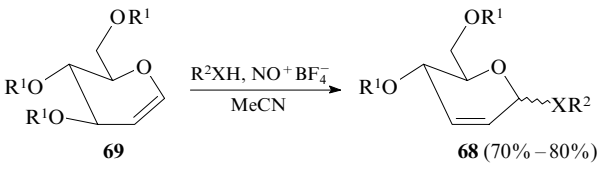
Scheme 15



R^2 = H: R^1 = 3-$O_2NC_6H_4$ (**a**), 4-$O_2NC_6H_4$ (**b**), 4-ClC_6H_4 (**c**), Ph (**d**), 2-HOC_6H_4 (**e**), Bn (**f**), 4-$MeOC_6H_4$ (**g**), 4-MeC_6H_4 (**h**);
R^2 = Me: R^1 = Ph (**i**), 4-BrC_6H_4 (**j**), 4-$MeOC_6H_4$ (**k**)

The nitrosonium cation was used as the oxidizing agent in the synthesis of hydroxysulfamide glycosides.[116] The reaction proceeds with high yield and high selectivity. The $NO^+BF_4^-$ salt is an efficient catalyst for the synthesis of 2,3-unsaturated 2-deoxyglycosides of alcohols, aryl thiols and aryl sulfonamides (**68**) from dihydropyrans **69** (Scheme 16).[117]

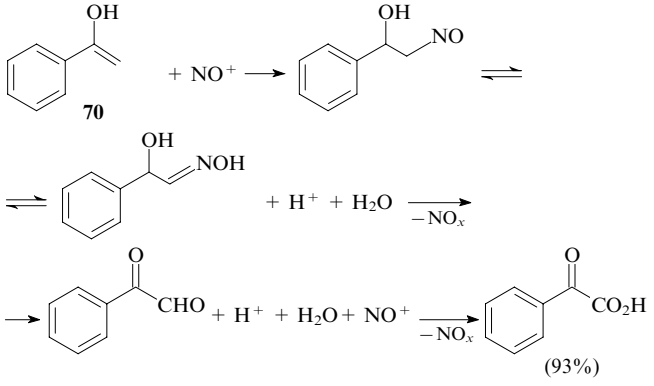
Scheme 16



R^1 = Acyl, Alk; R^2XH is alcohol, aryl thiol or aryl sulfonamide

Nitrosonium salts NO^+X^- [X = $B[3,5\text{-}(CF_3)_2C_6H_3]_4^-$ or $1/3(PW_{12}O_{40}^{3-})$] activate alkenes toward electrophilic arene alkylation and dimerization.[118] Marziano *et al.*[119] studied the oxidation of enolizable acetophenone (**70**) with nitric acid in aqueous sulfuric acid. It was hypothesized that the nitrosonium cation serves as an active oxidizing agent (Scheme 17).

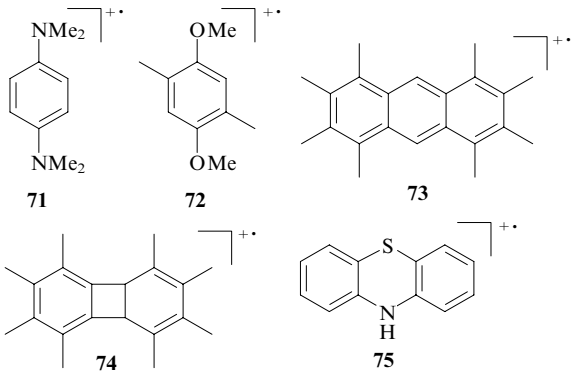
Scheme 17



III.2. Oxidation of aromatic and heterocyclic compounds with the NO^+ cation

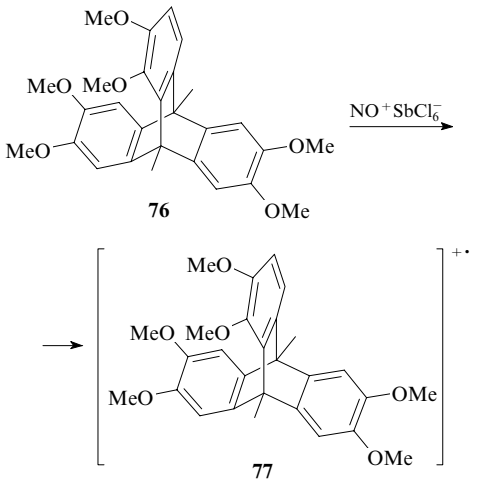
The nitrosonium cation is used as an oxidizing agent for aromatic and heterocyclic compounds. For instance, the reaction with $NO^+SbCl_6^-$ generated radical cations **71–75**. The rate constants for intermolecular electron transfer between these radical cations and precursors were evaluated.[120]

Structures 71–75



The reaction of $NO^+SbCl_6^-$ with dimethylhexamethoxytriptycene **76** at −10 °C in a CH_2Cl_2–PhMe mixture produces quite stable radical cation **77**, the structure of which was confirmed by X-ray diffraction (Scheme 18).[121]

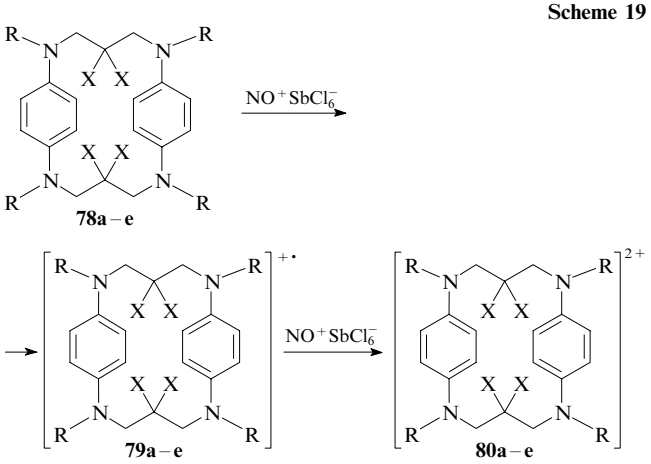
Scheme 18



The treatment of paracyclophanes **78a–e** with $NO^+SbCl_6^-$ in a molar ratio of 1 : 1 gave radical cations **79a–e**; an increase in the molar ratio to 1 : 2 resulted in the formation of dications **80a–e** in the singlet state; at X = H and R = Bn, the triplet state of dication **80d** being achievable under thermal conditions. The structures of dications **80a–e** were confirmed by X-ray diffraction (Scheme 19).[122–124]

The similar reaction of [8]cycloparaphenylene (**81**) with $NO^+SbF_6^-$ taken in a molar ratio of 1 : 1 produced radical cation **82**; an increase in the molar ratio to 1 : 5 resulted in the formation of dication **83** (Scheme 20).[125] The distinguishing feature of radical cation **82** is that its electronic

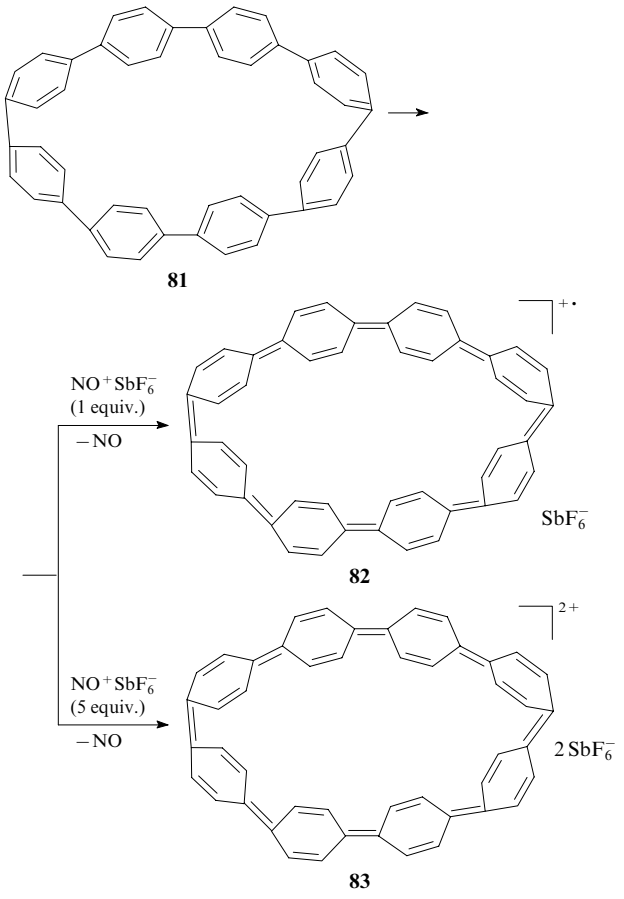
Scheme 19



X = H: R = Me (**a**), Et (**b**), Pr^i (**c**), Bn (**d**); X = R = Me (**e**)

absorption spectrum shows a long-wavelength band at 1102 nm.

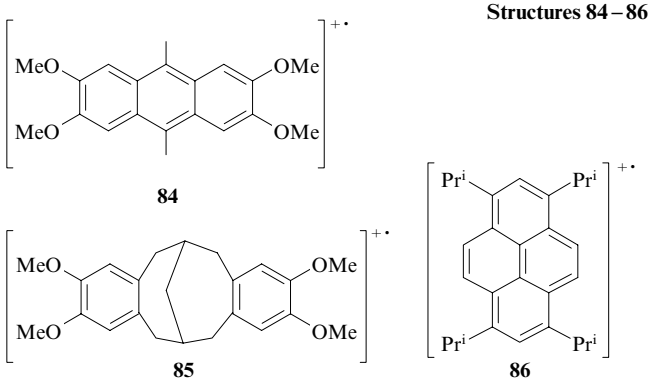
Scheme 20



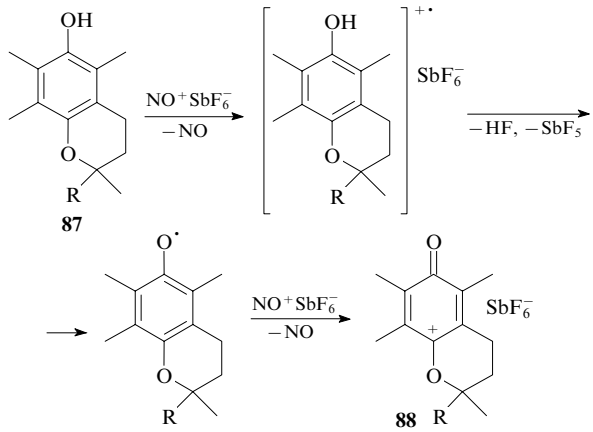
The oxidation of 9,10-dimethyl-2,3,6,7-tetramethoxyanthracene, tetramethoxydibenzobicyclo[4.4.1]undecane and 1,3,6,8-tetraisopropylpyrene with $NO^+SbCl_6^-$ in CH_2Cl_2 gives radical cations **84**–**86**, respectively.[126–128]

α-Tocopherol (**87**), which is the main component of vitamin E, is oxidized with $NO^+SbF_6^-$ (2 equiv.) in MeCN to phenoxonium cation **88** (Scheme 21).[129]

Structures 84–86



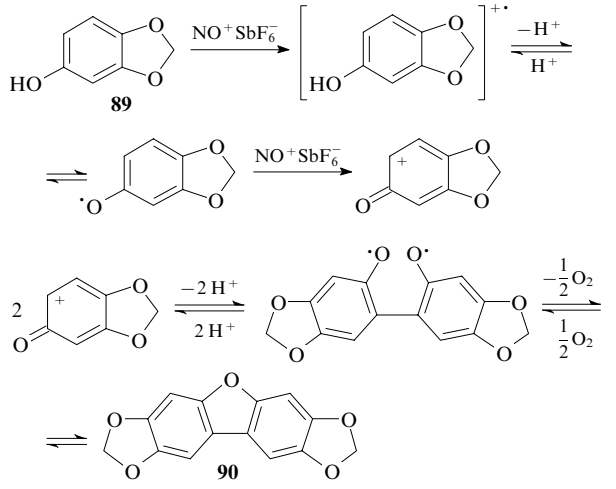
Scheme 21



R = $(CH_2)_3[CHMeCH_2CH_2CH_2]_2Pr^i$

The oxidation of sesamol (**89**) with an excess of $NO^+SbF_6^-$ affords dimer **90** in 18% yield.[130] The proposed reaction mechanism is shown in Scheme 22.

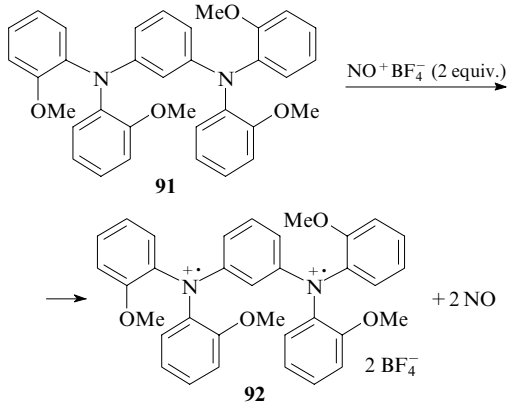
Scheme 22



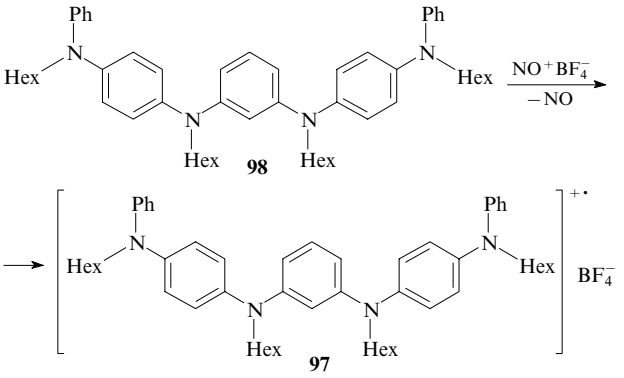
The NO^+X^- salts (X = BF_4, PF_6, AsF_6, $SbCl_6$) were used to oxidize aromatic compounds (naphthalene, anthracene, phenanthrene, pyrene, perylene, *etc.*) for the aryl–aryl bond formation, resulting in the preparation of dimeric products.[131] A method was developed for the cross-linking of organic semiconductors functionalized with oxetane moieties. The reaction was initiated by the addition of nitrosonium salts and irradiation of the sample at a wave-

length outside the absorption band of the onium salt.[132] The two-electron oxidation of *N*,*N*,*N*′,*N*′-tetrakis(2-methoxyphenyl)-1,3-diaminobenzene (**91**) with $NO^+BF_4^-$ in CH_2Cl_2 gives an aza analogue of Schlenk hydrocarbon — diradical dication **92** (Scheme 23).[133]

Scheme 23



Scheme 24

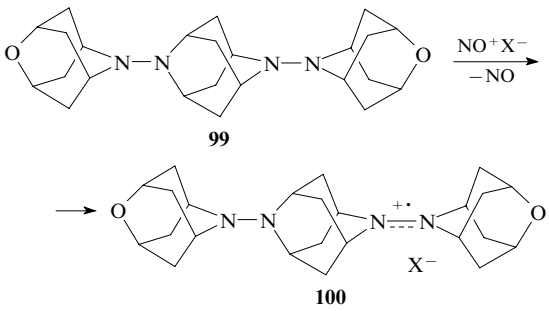


However, attempts to use this method for the synthesis of tetraradical tetracations from compounds **93** and **94** failed. The oxidation of poly{2-[bis(4-methoxyphenyl)amino]phenyl-5-(2-ethylhexyloxy)-1,4-phenylenevinylene} with $NO^+PF_6^-$ in CH_2Cl_2 gives azaniumyl poly(radical cation) **95** with a half-life of approximately two weeks.[134] The spin concentration estimated by EPR spectroscopy for this radical cation and its model analogue **96** is 0.34 (per monomer unit) and 0.94, respectively.

Radical cation **97**, which was generated from arylamine **98** on treatment with $NO^+BF_4^-$, is quite stable in an acid medium (Scheme 24).[135]

The oxidation of 2,6-bis(2′-oxa-6′-azaadamantan-6′-yl)-2,6-diazaadamantane (**99**) with nitrosonium salts affords radical cation **100**, in which, as evidenced by EPR, the charge is located at one of the hydrazine moieties (Scheme 25).[136]

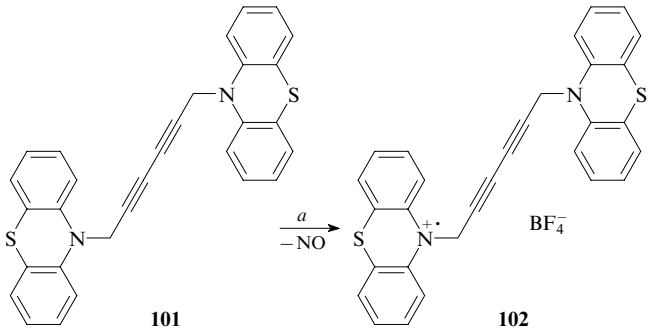
Scheme 25



X = Br_4, PF_6, SbF_6

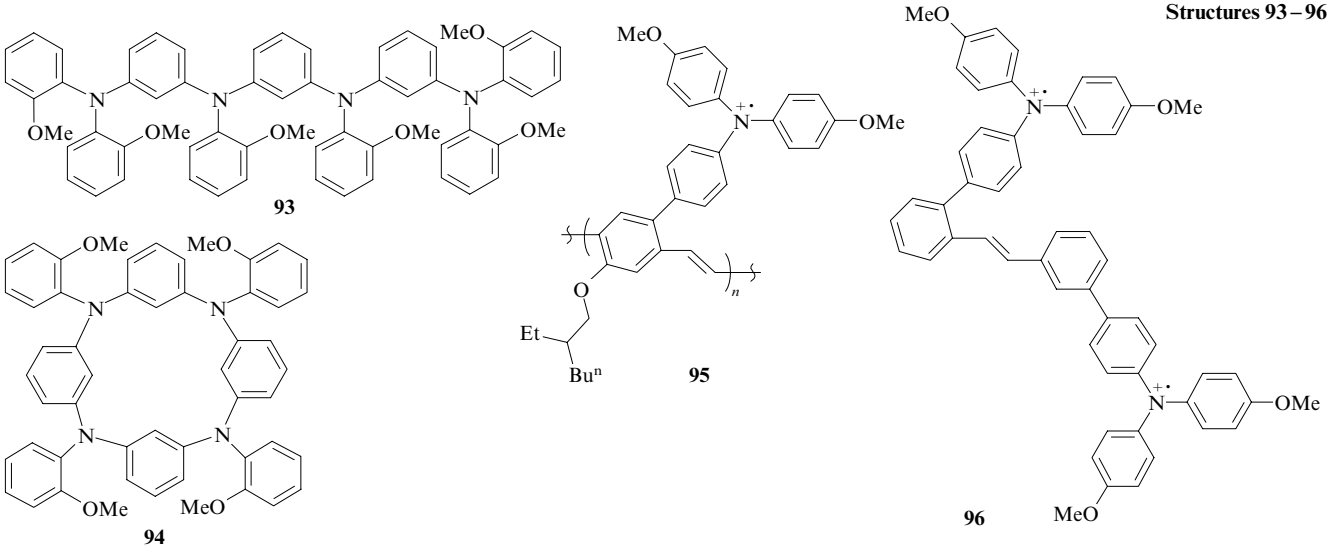
The oxidation of 1,6-bis(phenothiazino)hexa-2,4-diyne (**101**) with $NO^+BF_4^-$ to radical cation **102** occurs at low temperature and is accompanied by the release of NO (Scheme 26).[137]

Scheme 26



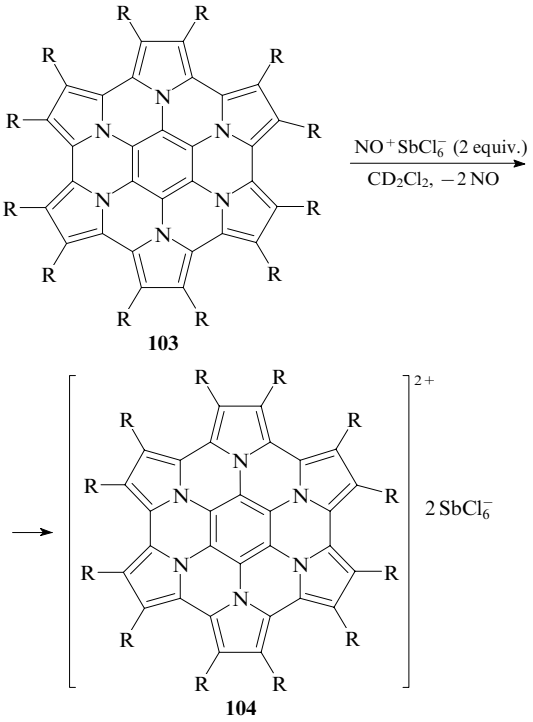
(*a*) $NO^+BF_4^-$, CH_2Cl_2, −40 °C

Structures 93–96



The treatment of aryl-substituted hexapyrrolohexaazacoronene **103** with an excess of $NO^+SbCl_6^-$ in CD_2Cl_2 produces dication **104**, the structure of which was confirmed by ^1H and ^{13}C NMR spectroscopy and X-ray diffraction (Scheme 27).[138]

Scheme 27



103

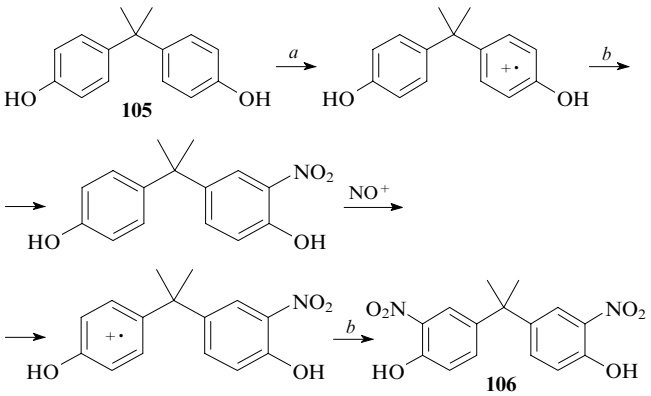
104

R = 4-$F_3CC_6H_4$

Efficient methods were developed for the oxidation of benzyl alcohol to benzaldehyde using the $NaNO_2$–acid[139] or isoamyl nitrite–sulfonic acid system.[140] Evidently, the reactions proceed with the participation of the NO^+ cation. The oxidation of propane-1,2-diol with divalent metal (Co^{II}, Ni^{II}, Cu^{II}) nitrates yields the hydroxy acid $MeCH(OH)CO_2H$. The proposed mechanism resulting in the formation of this acid also involves the NO^+ cation.[141, 142]

The treatment of bisphenol **105** with $NO^+SbF_6^-$ in a $MeCN-H_2O$ mixture gives 4,4′-(propane-2,2′-diyl)bis(2-nitrophenol) (**106**) in 9% yield (Scheme 28).[143] The formation of the nitro product requires the participation of oxygen.

Scheme 28



105

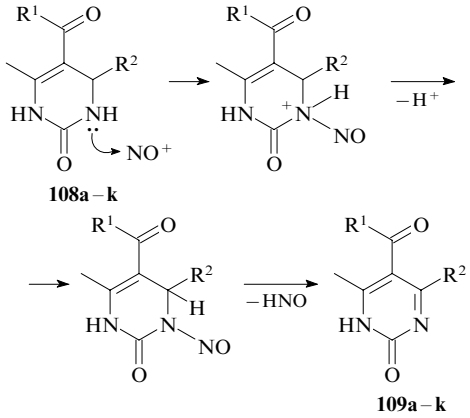
106

(*a*) NO^+, $-NO$; (*b*) NO_2, $-H^+$

$$NO + \frac{1}{2}O_2 \longrightarrow NO_2$$

The oxidation of thianthrene with $NO^+BF_4^-$ in MeCN or with $NO^+PF_6^-$ in Bu^nCN produced thianthrene radical cation **107**.[144, 145] 3,4-Dihydropyrimidin-2(1*H*)-ones **108a–k** were oxidized with $NO^+BF_4^-$ in acetonitrile at room temperature to pyrimidin-2(1*H*)-ones **109a–k** (yields >99%) (Scheme 29).[146]

Scheme 29



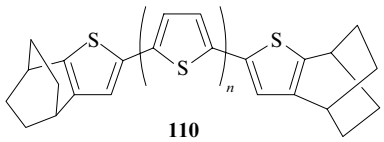
108a–k

109a–k

R^1 = EtO: R^2 = Pr^n (**a**), Bu^i (**b**), Hex (**c**), Ph (**d**), 2-MeC_6H_4 (**e**), 4-MeC_6H_4 (**f**), 4-$MeOC_6H_4$ (**g**), 4-ClC_6H_4 (**h**), 4-$O_2NC_6H_4$ (**i**);
R^1 = Me: R^2 = Ph (**j**), 4-MeC_6H_4 (**k**)

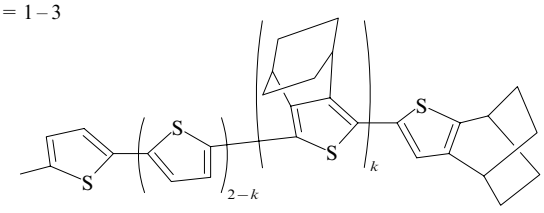
The reaction of oligothiophenes **110** and **111** with $NO^+SbF_6^-$ in CH_2Cl_2 gives radical cations, the radical cations that are generated from oligomers **110** (n = 2, 3) and **111** (k = 0, 1) forming dimers at low temperatures.[147]

Structures 110, 111



110

n = 1–3



111

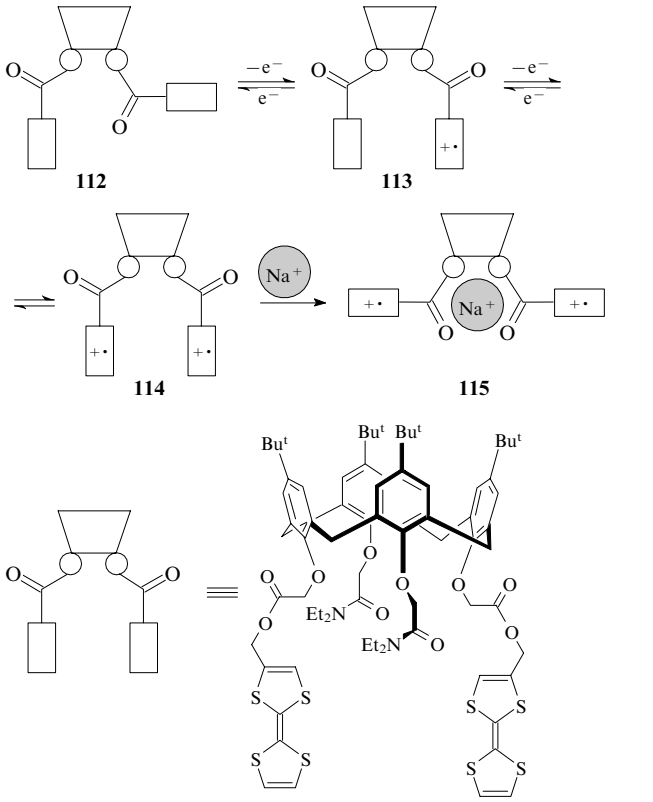
k = 0–2

The oxidation of calix[4]arene–TTF assemblies **112** (TTF is tetrathiafulvalene) with $NO^+SbF_6^-$ affords radical cations **113** and **114**. The addition of $NaClO_4$ results in the formation of complex **115** and the disappearance of an absorption band at 1750 nm in the electronic absorption spectrum assigned to $[(TTF)_2]^{+\cdot}$ dimers (radical cation **113**) (Scheme 30).[148]

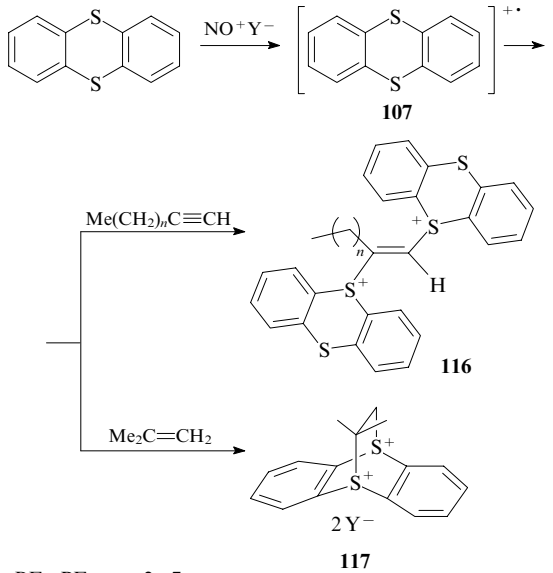
The thianthrene radical cation (**107**), which was prepared by oxidation of thianthrene with $NO^+BF_4^-$ or $NO^+PF_6^-$, reacted with alkynes to give dications **116** and with isobutene to yield adduct **117** (Scheme 31).[149, 150]

The one-electron oxidation of dialkyl diselenides **118a**,**b** and dialkyl ditellurides **118c–e** with the $NO^+CF_3SO_3^-$ salt

Scheme 30



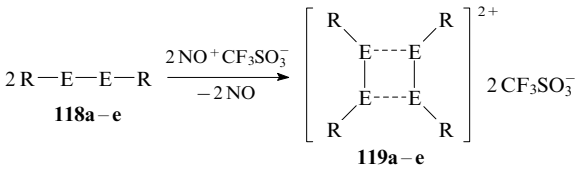
Scheme 31



Y = BF_4, PF_6; n = 2–7

affords the dimers $[AlkSe]_4^{2+}$ (**119a**,**b**) and $[AlkTe]_4^{2+}$ (**119c**–**e**), respectively (Scheme 32).[151] *Ab initio* calculations (MP2 method) provided evidence for the *trans*-arrangement of alkyl groups in the resulting radical cations. The presence of four-centre six-electron $(Se\cdots Se)_2$ and $(Te\cdots Te)_2$ bonds in the dimers is attributed to the so-called $\pi^*-\pi^*$ interaction.

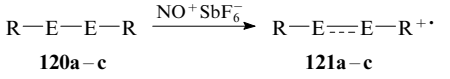
Scheme 32



E = Se: R = Me (**a**), Et (**b**); E = Te: R = Et (**c**), Pr^n (**d**), Bu^i (**e**)

As opposed to the above reactions, the oxidation of diaryl dichalcogenides **120a**–**c** with $NO^+SbF_6^-$ does not give dimers; instead, this reaction affords quite stable radical cations **121a**–**c** (Scheme 33).[152]

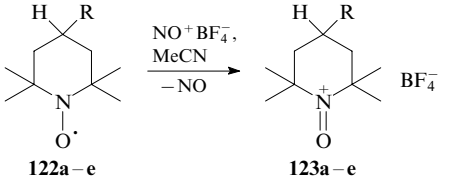
Scheme 33



R = 2,6-$Mes_2C_6H_3$: E = S (**a**), Se (**b**), Te (**c**); Mes = 2,4,6-$Me_3C_6H_2$

Studies by multinuclear magnetic resonance spectroscopy (^1H, ^{13}C, ^{19}F and ^{14}N) demonstrated that 4-substituted 2,2,6,6-tetramethylpiperidine-1-oxyl radicals **122a**–**e** are oxidized with $NO^+BF_4^-$ to 2,2,6,6-tetramethyl-1-oxopiperidinium cations **122a**–**e** (Scheme 34).[153]

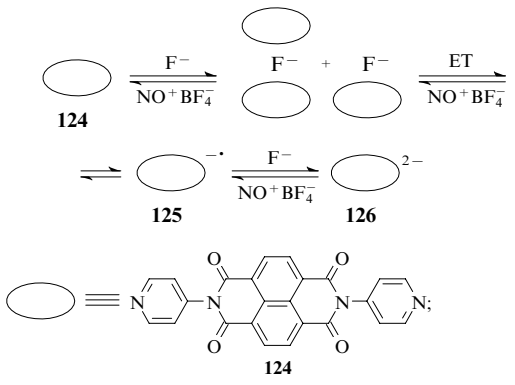
Scheme 34



R = H (**a**), OH (**b**), OMe (**c**), OBz (**d**), NHAc (**e**)

The $NO^+BF_4^-$ salt was used as an oxidizing agent to study the supramolecular reaction of the F^- anion with naphthalene-1,4,5,8-tetracarboxylic acid diimide (**124**), which can be employed as a sensor for fluoride (Scheme 35).[154] The addition of $NO^+BF_4^-$ to solutions of radical anion **125** and anion **126** (orange and pink colour, respectively) leads to bleaching of these solutions.

Scheme 35



ET is electron transfer ($F^- \rightarrow$ **124**)

Thus, nitrosonium salts can be used as oxidizing agents for different classes of organic compounds, including free radicals, radical anions and dianions.

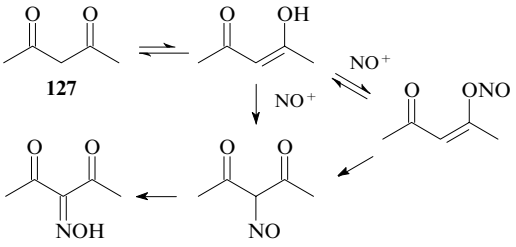
IV. Nitrosation reactions involving the NO^+ cation

Nitrosation reactions of organic compounds are considered in sufficient detail in a monograph,[13] which covers publications up to 2003. The influence of cyclodextrins on the nitrosation of organic and bioorganic molecules was analyzed in a review.[155] The present review is focused on more recent publications.

IV.1. Nitrosation at carbon atom

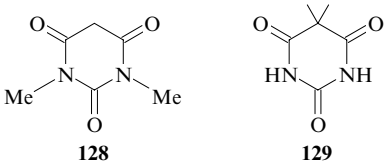
Investigations of the kinetics of nitrosation of acetylacetone (**127**) demonstrated that the reaction proceeds through two pathways — at carbon and oxygen atoms *via* nucleophilic and acid-base catalysis, respectively (Scheme 36).[156, 157]

Scheme 36



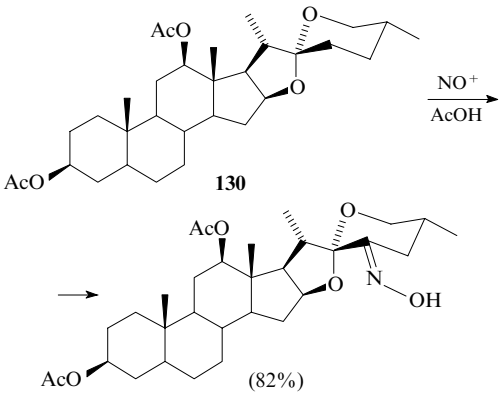
The use of methyl-substituted barbituric acids **128** and **129** as models showed that the attack on the enol carbon atom is the rate-limiting step in C-nitrosation, whereas the proton transfer is the rate-limiting step in O-nitrosation.[158]

Structures 128, 129



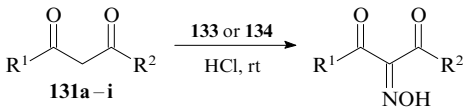
The *in situ* generated nitrosonium cation (Bu^tONO, $BF_3 \cdot Et_2O$) is an effective oximinylating agent for enol ethers derived from steroidal spiroketals, for example, of compound **130** (Scheme 37).[159]

Scheme 37



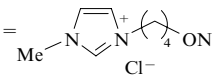
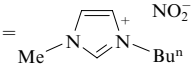
β-Dicarbonyl compounds **131a–i** were transformed into corresponding oxyaminoketones **132a–i** using nitrite ionic liquids and HCl (Scheme 38).[160]

Scheme 38



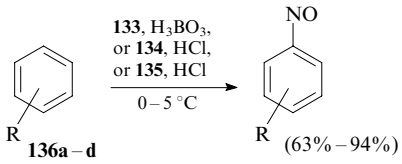
132a–i (63%–95%)

R^1 = Me: R^2 = Ph (**a**), OMe (**b**), Bn (**c**); $R^1 = Pr^n$, R^2 = OMe (**d**); $R^1 = R^2$ = Me (**e**), Et (**f**), Ph (**g**), OMe (**h**), NH_2 (**i**);

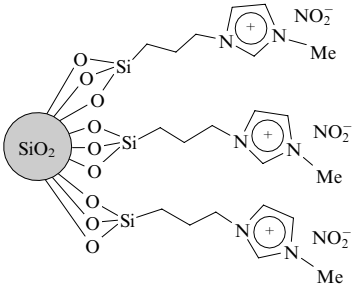
133 =  , **134** =  ([bmim]NO_2);

Nitrite ionic liquids **133–135** were employed also for nitrosation of substituted benzenes **136a–d** (Scheme 39).[161, 162]

Scheme 39

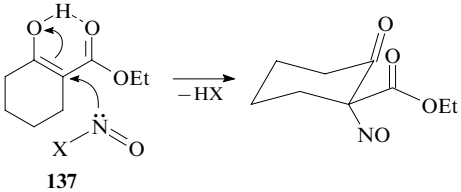


R = OH (**a**), OMe (**b**), NMe_2 (**c**), NEt_2 (**d**), *etc.*;

135 = 

The nitrosation of the enol tautomer of ethyl 2-oxocyclohexanecarboxylate (**137**) (Scheme 40) is inhibited by β-cyclodextrin because of the formation of an unreactive host–guest complex.[163]

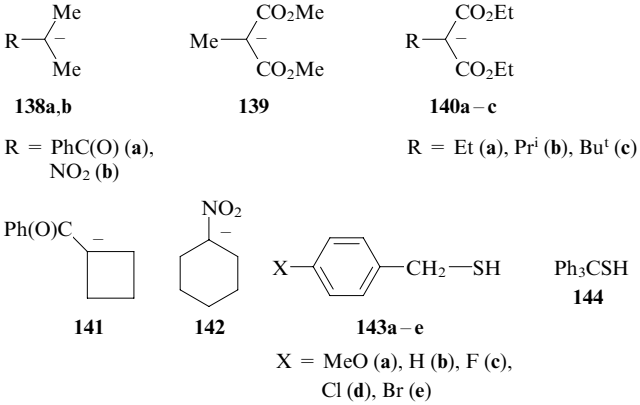
Scheme 40



X = H_2O, Cl^-, Br^-, SCN^-

The heats of reactions of carbanions **138ab**, **139**, **140a–c**, **141**, **142** and thiols **143a–e**, **144** with $NO^+ClO_4^-$ in MeCN were determined by calorimetry.[164] The tendency to the transfer of the NO group from C-nitroso compounds to thiols was assessed based on thermodynamic data.

Structures 138–144



138a,**b** **139** **140a–c**

R = PhC(O) (**a**), NO_2 (**b**)

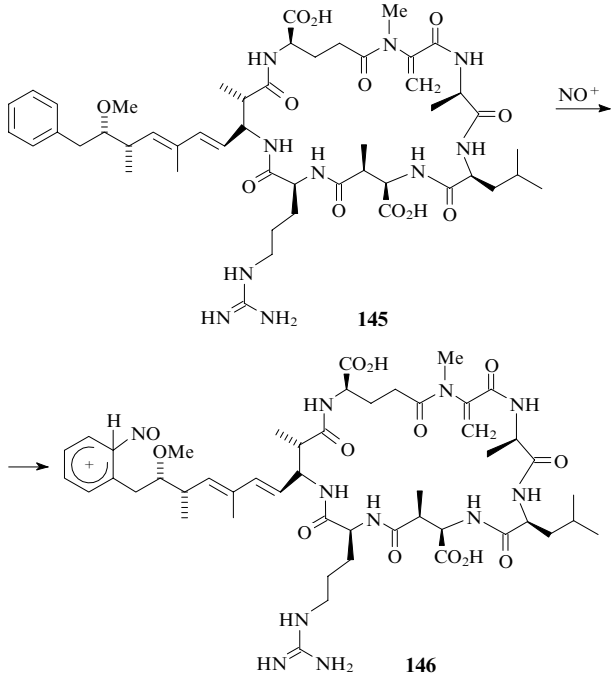
R = Et (**a**), Pr^i (**b**), Bu^t (**c**)

141 **142** **143a–e** **144**

X = MeO (**a**), H (**b**), F (**c**), Cl (**d**), Br (**e**)

Ma *et al.*[165] investigated the kinetics and mechanism of the reaction of microcystin-LR **145** with nitrous acid. The authors proposed the reaction mechanism involving nitrosonium σ-complex **146** for the formation of the C-nitroso product (Scheme 41). Unfortunately, the σ-complex and the product were identified only by LC-MS [*m*/*z* 512.8 (*M* 1024.5) and 1024.5 (*M* 1023.5), respectively], which is obviously insufficient for the establishment of their structures. Taking into account the presence of reactive NH groups in the substrate, this mechanism is unlikely for C-nitrosation.

Scheme 41



145 **146**

Aryl and hetaryl trifluoroborates **147–152** undergo *ipso*-substitution under mild conditions when treated with $NO^+BF_4^-$ to give nitroso products in high yields (72%–96%) (Scheme 42).[166]

Scheme 42

147a–h, **148–152**

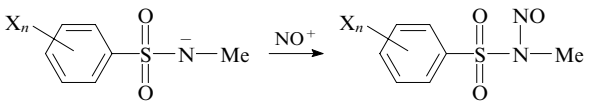
for **147**: R = 4-Bu^tC$_6$H$_4$ (**a**), 4-PhC$_6$H$_4$ (**b**), 3-MeOC$_6$H$_4$ (**c**), 4-MeOC$_6$H$_4$ (**d**), 4-BnOC$_6$H$_4$ (**e**), 4-MeO$_2$CC$_6$H$_4$ (**f**), 2-CHOC$_6$H$_4$ (**g**), 2,4-(MeO)$_2$C$_6$H$_3$ (**h**);

R = (**148**), (**149**), [E = O (**150a**), S (**150b**)], (**151**), (**152**)

IV.2. Nitrosation at nitrogen atom

N-Methylbenzenesulfonamide anions **153a–g**, which are generated by the proton abstraction from appropriate sulfonamides under the treatment with KH, quantitatively react with $NO^+ClO_4^-$ in MeCN to give substituted *N*-methyl-*N*-nitrosobenzenesulfonamides **154a–g** (Scheme 43).[167] The energy of the heterolytic N–NO bond cleavage in these compounds decreases with an increase in the electron-withdrawing character of the substituent X.

Scheme 43



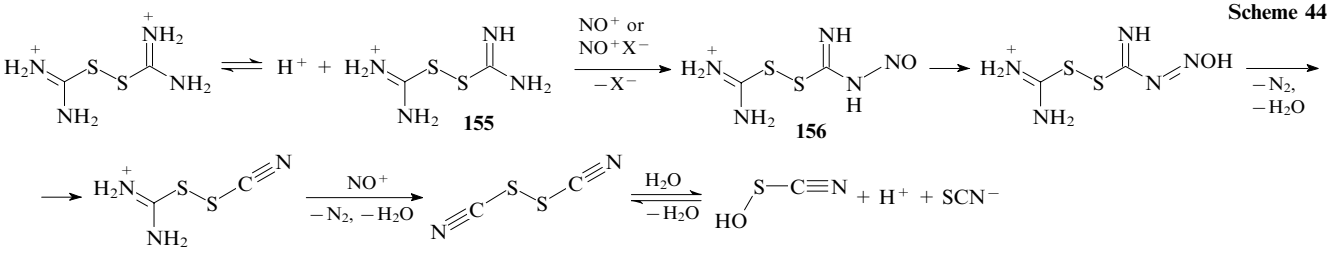
153a–g **154a–g**

X_n = 4-OMe (**a**), 4-Me (**b**), H (**c**), 4-Cl (**d**), 4-Br (**e**), 3-NO_2 (**f**), 2,5-Cl_2 (**g**)

The attack of nitrosating agents (NOCl, NOBr or NOSCN) giving rise to nitroso derivative **156** is the rate-limiting step of nitrosation of protonated formamidine disulfide **155** in an acid medium (Scheme 44).[168] An analysis of the kinetic data demonstrated that the reaction is autocatalyzed due to the formation of thiocyanate. The addition of a nucleophile suppresses the autocatalysis.

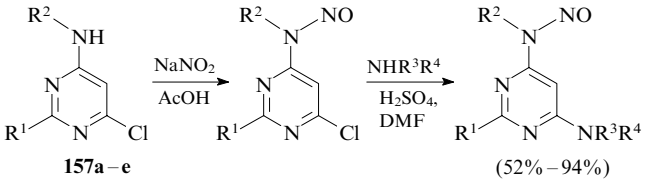
The absence of general base catalysis, the presence of catalysis by anions (X^- and SCN^-) and the observed inverse kinetic isotope effect, [$k(H_2O)/k(D_2O) = 0.5$, suggest that the electrophilic attack of the nitrosating agent (NO^+ or NOX) is the rate-limiting step of nitrosation of aminoguanidine.[169] The kinetics of nitrosation of aniline derivatives with different nitrosating agents, such as NOCl, NOBr, N_2O_3, NOSCN, NOI, $NOSC(NH_2)_2$ and NOS_2O_3, was investigated.[170] An analysis of the kinetic data in terms

Scheme 44



155 **156**

Scheme 45

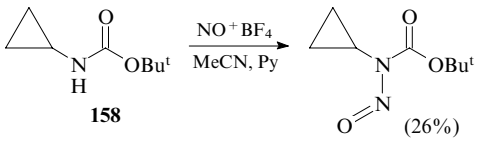


R^1 = H: R^2 = Me (**a**), Bu^n (**b**), $CH_2CH{=}CH_2$ (**c**), Bn (**d**);
R^1 = Me, R^2 = Bn (**e**); R^3 = R^4 = Et; R^3-R^4 = $(CH_2)_4$;
R^3 = H: R^4 = Bn, 4-$MeOC_6H_4$, *etc.*

of the Marcus, Brønsted and Leffler equations provides evidence that the intrinsic barrier to reaction is low and that the transition state is similar to the reaction product. The kinetics of nitrosation of novocaine in a mild acid medium follows the equation that contains first- and second-order terms with respect to the nitrite concentration, which corresponds to two parallel reaction pathways (involving the NO^+ cation and N_2O_3, respectively). The reaction rate increases with an increase in the acidity of the medium.[171] The introduction of the N-nitroso group into chloropyrimidines **157a–e** under the treatment with $NaNO_2$ in AcOH was used to activate the nucleophilic substitution of a chlorine atom by amino groups (Scheme 45).[172]

The cyclopropyl group remains intact upon nitrosation of *tert*-butyl cyclopropylcarbamate (**158**) with $NO^+BF_4^-$ (Scheme 46).[173]

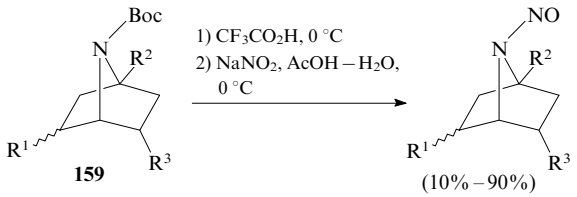
Scheme 46



Py is pyridine

The core of 7-azabicyclo[2.2.1]heptanes **159** also remains intact upon nitrosation with the $NaNO_2-AcOH-H_2O$ system (Scheme 47).[174]

Scheme 47

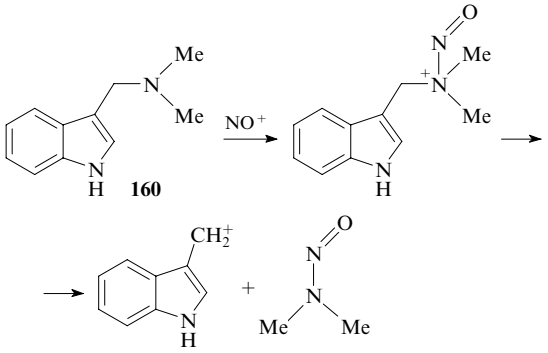


R^1 = H, CO_2Me; R^2 = H, CH_2OMe; R^3 = H, CO_2Me, CO_2Bn;
Boc = C(O)OBu^t

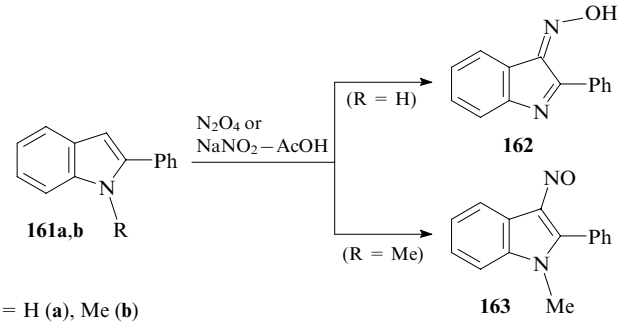
Shojaie and Dehestani[175] studied the mechanism of the reaction of gramine (**160**) with the nitrosonium cation (Scheme 48) at the B3LYP/6-311+G(d,p) level of theory, the results of quantum chemical calculations being in good agreements with the experimental data.

The reaction of N_2O_4 or $NaNO_2-AcOH$ with 2-phenylindole (**161a**) and 1-methyl-2-phenylindole (**161b**) affords 2-phenylindol-3-one oxime (**162**) and 1-methyl-3-nitroso-2-phenyl-1*H*-indole (**163**), respectively (Scheme 49).[176]

Scheme 48



Scheme 49

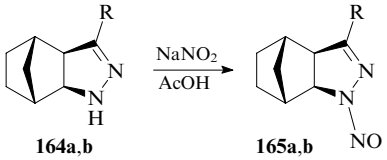


R = H (**a**), Me (**b**)

The reaction of 3,4-diazatricyclo[5.2.1.$0^{2,6}$]dec-4-ene (**164a**) with $NaNO_2-AcOH$ at 0 °C produces 3-nitroso-3,4-diazatricyclo[5.2.1.$0^{2,6}$]dec-4-ene (**165a**) in 46% yield (Scheme 50).[177]

The reaction pathway of nitrosation remains unchanged after the replacement of a hydrogen atom at position 3 of compound **164a** by the CO_2Me group.

Scheme 50

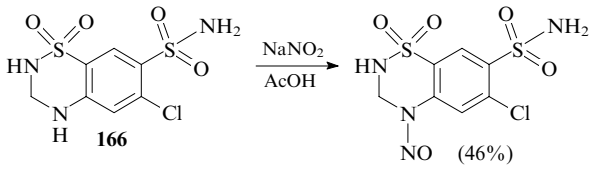


R = H (**a**), CO_2Me (**b**)

The treatment of methyl *exo*-3,4-diazatricyclo[5.2.1.$0^{2,6}$]-dec-4-ene-5-carboxylate (**164b**) with $NaNO_2-AcOH$ affords methyl 3-nitroso-*exo*-3,4-diazatricyclo[5.2.1.$0^{2,6}$]dec-4-ene-5-carboxylate (**165b**) in 70% yield (see Scheme 50).[178]

The nitrosation of 6-chloro-3,4-dihydro-2*H*-1,2,4-benzothiadiazine-7-sulfonamide 1,1-dioxide (**166**) with $NaNO_2$ in AcOH occurs at the N(4) atom, which is a stronger nucleophilic centre than the N(2) atom or the NH_2 group (Scheme 51).[179]

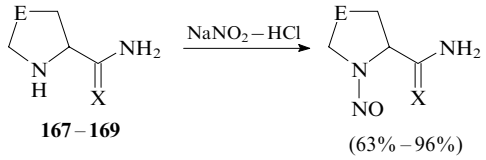
Scheme 51



The nitrosation of pyrrolidine-2-thiocarboxamide (**167**), 1,3-thiazolidine-4-carboxamide (**168**) and 1,3-thiazolidine-

4-thiocarboxamide (**169**) with $NaNO_2-HCl$ occurs at the endocyclic nitrogen atom due evidently to higher nucleophilicity of this atom compared with the O, S and NH_2 centres (Scheme 52).[180]

Scheme 52



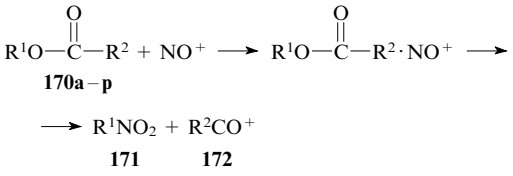
167–169

E = CH_2, X = S (**167**); E = S: X = O (**168**), S (**169**)

IV.3. Nitrosation at O and S atoms

The $NO^+BF_4^-$ salt reacts with benzyl alcohol in $CDCl_3$ in the presence of 2,6-di(*tert*-butyl)-4-methylpyridine to give benzyl nitrite.[181] The antidote to cyanide poisoning — 3-methylbutyl nitrite — was synthesized by the reaction of 3-methylbutan-1-ol with $NaNO_2$, which serves as a source of NO^+, in the presence of the $Fe_3O_4@SO_3H$ catalyst.[182] The reactivity of N_2O_3 as an oxidizer was tested in the catalytic oxidation of alcohols and the methyl group of acetophenone.[183] The nitrosonium cation was considered as the reactive species, which was detected by Raman spectroscopy on the $H_2SO_4-SiO_2$ catalyst. The reactions of the nitrosonium cation with esters **170a–p** in the gas phase lead to the C–O bond cleavage and the formation of nitroalkanes **171** and acylium cations **172** (Scheme 53).[184] Unfortunately, the authors did not mention the source of nitrosonium cations.

Scheme 53



170a–p **171** **172**

R^1 = Me: R^2 = Bu^n (**a**), Hex (**b**); R^1 = Et: R^2 = MeCH=CH (**c**), Pr^n (**d**), Bu^n (**e**); R^1 = Pr^n: R^2 = Pr^i (**f**); R^1 = Bu^n: R^2 = Me (**g**), Et (**h**), Pr^n (**i**); R^1 = Bu^i: R^2 = Me (**k**), Pr^n (**l**), Pr^i (**m**); R^2 = Me: R^1 = n-C_5H_{11} (**n**), CH_2=CH$(CH_2)_4$ (**o**), EtCH=CH$(CH_2)_2$ (**p**)

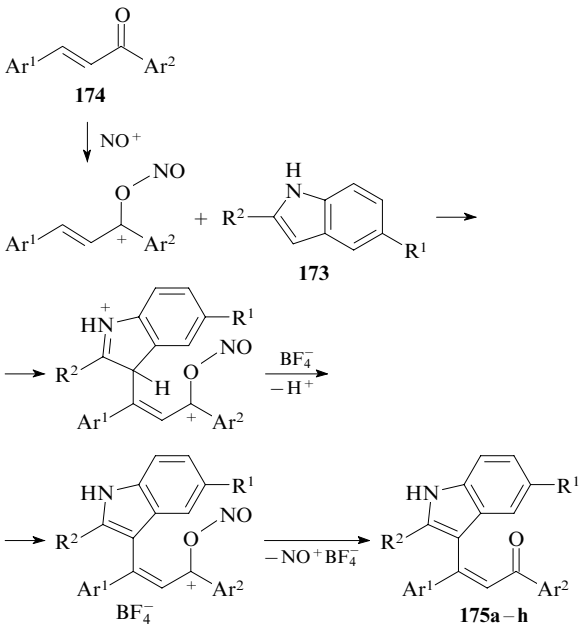
The Michael addition of indoles **173** to unsaturated enones **174** in the presence of a catalytic amount of $NO^+BF_4^-$ gave products **175a–h** in 93%–99% yields (Scheme 54).[185]

The nitrosation of 2-aminoethanethiol with the acid HNO_2 occurs at the sulfur atom rather than at the nitrogen atom to give $H_2NCH_2CH_2SNO$.[186] The nitrosation of homocysteine (**176**) with nitrous acid [reaction (1)] proceeds in a similar way.[187] The bimolecular rate constants of nitrosation of homocysteine with HNO_2, N_2O_3 and NO^+ are 9.0×10^{-2}, 9.50×10^{3} and 6.57×10^{10} litre mol^{-1} s^{-1}, respectively. These data are consistent with an order of electrophilicity for these reagents ($HNO_2 < N_2O_3 < NO^+$).

$$H_2NCH(CO_2H)CH_2CH_2SH + HNO_2 \longrightarrow H_2NCH(CO_2H)CH_2CH_2SNO + H_2O \quad (1)$$

176

Scheme 54



175a–h

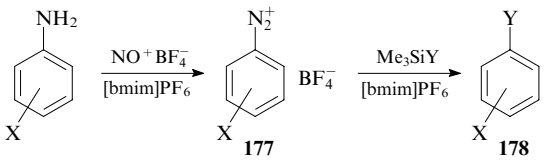
Compound **175**	Ar^1	Ar^2	R^1	R^2
a	Ph	Ph	H	H
b	Ph	Ph	H	Me
c	Ph	Ph	MeO	H
d	Ph	Ph	O_2N	H
e	4-ClC_6H_4	Ph	H	Me
f	Ph	4-$MeOC_6H_4$	H	Me
g	Ph	4-BrC_6H_4	H	Me
h	4-ClC_6H_4	4-$MeOC_6H_4$	H	Me

The bimolecular rate constant of nitrosation of captopril with NO^+ in an acid medium is much higher compared with N_2O_3, which attests to higher electrophilicity of NO^+.[188] A method was developed for the synthesis of unstable, highly reactive S-nitroso thioacids RC(O)SNO based on the nitrosation of thioacids RC(O)SH with amyl nitrite, $HCl-NaNO_2$ or a nitrosonium salt. These nitroso thioacids were employed in the synthesis of amides and peptides.[189]

V. Diazotization of amines and their derivatives

Nitrosonium salts are widely used in the diazotization of aromatic amines. The treatment of substituted anilines with $NO^+BF_4^-$ produced aryl diazonium salts **177**, which reacted with Me_3SiY (Y = Br, I, N_3) to give bromo-, iodo- and azidoaromatic derivatives **178** (Scheme 55).[190]

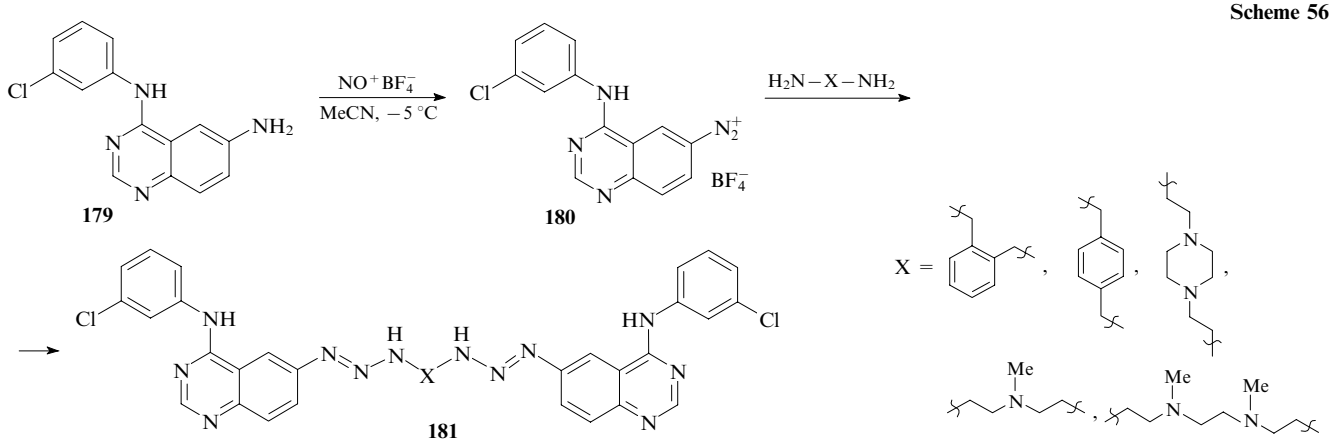
Scheme 55



177 **178**

X = H, 4-Me, 4-Bu^t, 4-OMe, 4-Cl, 4-Br, 3-NO_2; Y = Br, I, N_3

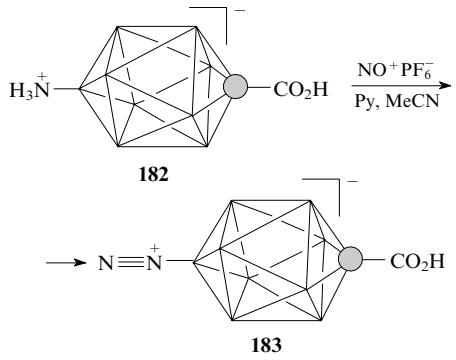
Scheme 56



The reaction of $NO^+BF_4^-$ with 6-amino-4-(3-chlorophenylamino)quinazoline (**179**) in MeCN affords diazonium salt **180**. The latter reacts with $H_2N-X-NH_2$ compounds to form derivatives **181**, in which two aminoquinazoline moieties are connected by a linker. Compounds **181** exhibit antitumour activity (Scheme 56).[191]

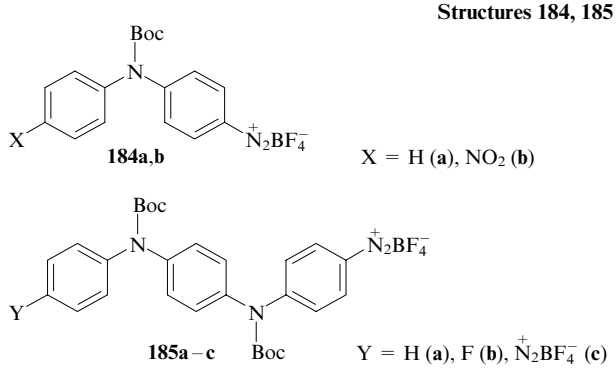
2,6-Dimethylbenzenediazonium tetrafluoroborate, which was produced by the treatment of 2,6-dimethylaniline with $NO^+BF_4^-$, was used to generate radicals from AlkI grafted to carbon surfaces.[192] The reaction of $NO^+PF_6^-$ with carborane **182** at −20 °C was applied to synthesize diazonium salt **183** (Scheme 57).[193]

Scheme 57



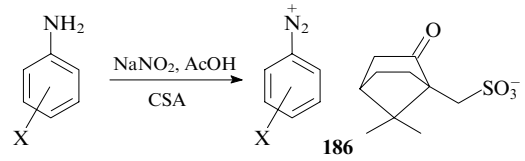
Diazonium salts **184a**,**b** and **185a**–**c**, which were prepared by the reaction of aromatic amines with $NO^+BF_4^-$ or $Bu^tONO-BF_3\cdot OEt_2$, can be employed to fabricate monolayers on silicon surfaces.[194]

Structures 184, 185



A series of stable arenediazonium camphorsulfonate salts **186** were synthesized by diazotization of substituted anilines (Scheme 58) and were used to prepare aryl halides and as DNA cleaving agents.[195]

Scheme 58



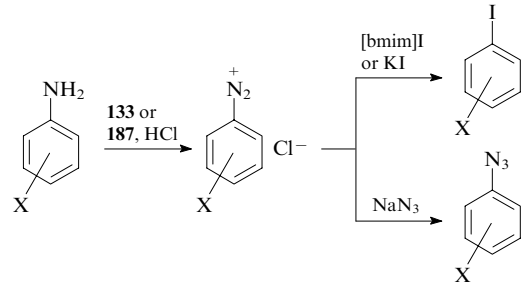
X = 4-OMe, 2-CN, 4-CN, 2-Br, 4-Br, 4-Cl, 4-I, 2-NO_2, 3-NO_2, 4-NO_2; CSA is camphorsulfonic acid

Velasco *et al.*[196] described a method for the synthesis of aryl diazonium salts using $Fe(NO_3)_3\cdot 9H_2O$ and HCl in MeCN.

Recently, nitrite ionic liquids, including those attached to substrates, have been proposed as nitrosonium cation sources.

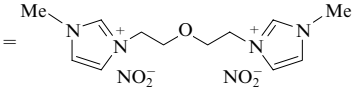
The ionic liquid (IL) 3-methyl-1-(4-nitritobutyl)imidazolinium chloride coupled with HCl is an efficient reagent for diazotization of amines $XC_6H_4NH_2$ (X = H, 4-OH, 4-NO_2).[197] A procedure was developed for the synthesis of aryl iodides and aryl azides *via* diazotization of appropriate arylamines using nitrite ionic liquids (for example, IL **133** or **187**) followed by the replacement of the N_2^+ group by the I atom or the N_3 group (Scheme 59).[9,198]

Scheme 59



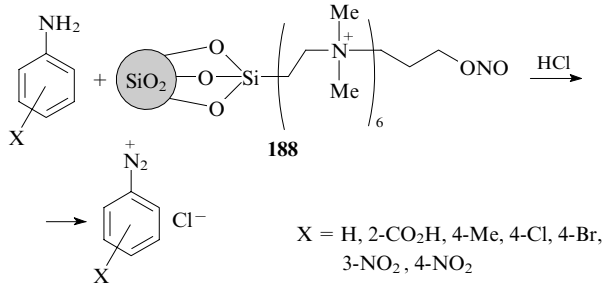
X = H, 2-Cl, 4-Ac, 2-NO_2, 4-NO_2, *etc.*;

187 =



Nitrite-functionalized polyionic organosilicon compound **188** was also employed as a NO^+ source for diazotization of aniline derivatives (Scheme 60).[199]

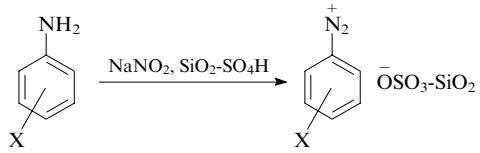
Scheme 60



X = H, 2-CO_2H, 4-Me, 4-Cl, 4-Br, 3-NO_2, 4-NO_2

An efficient method was developed for the synthesis of aryl diazonium salts using sulfuric acid-modified silica gel (silica sulfuric acid) under solvent-free conditions (Scheme 61).[200]

Scheme 61



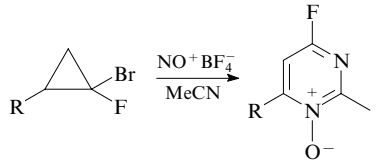
X = H, 2-Me, 2-Cl, 3-Cl, 2-NO_2, 4-NO_2, 4-SO_3Na

Graphene functionalized with ONO groups (jointly with OH, CO_2H, $CO_2^-Na^+$) is an effective nitrosonium cation source and was employed for diazotization of a wide range of aromatic amines.[201]

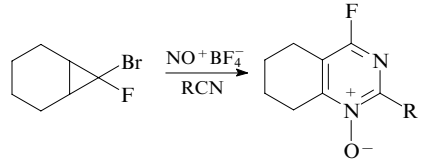
VI. Nitrosonium cation in the synthesis of heterocyclic compounds

Nitrosonium salts are of interest as reagents for heterocyclization of a series of cyclopropane derivatives. Reactions of alkyl-substituted *gem*-dichlorocyclopropanes with $NOAlCl_4$ or $NOCl \cdot 2\,SO_3$ produce mixtures of regioisomeric 3-alkyl- and 4-alkyl-5-chloroisoxazoles.[202, 203] In the presence of alkylnitriles, halogen-substituted cyclopropanes give pyridine *N*-oxides in 33%–80% yields (Scheme 62).[204, 205]

Scheme 62



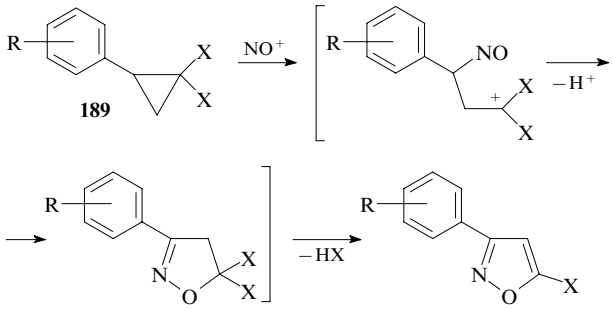
R = Bu^n, Bn, Ph, 3-ClC_6H_4, *etc.*



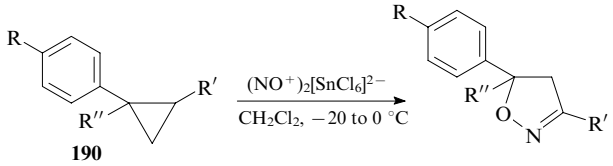
R = Me, Et, Bu^t, CH_2CN, $(CH_2)_2OMe$, $(CH_2)_3Cl$, Ph, *etc.*

The nitrosation of 1-phenyl-2-R-cyclopropanes containing bulky alkyl substituents (R = Pr^i, Bu^t, cyclo-C_6H_{11}) with $NOCl \cdot 2\,SO_3$ proceeds predominantly *via* the attack of the nitrosonium cation on the benzylic carbon atom to form isoxazolines, 1,2-oxazines and Δ^1-pyrroline *N*-oxide.[206] The heterocyclization of 2-aryl-1,1-dichloro- and -1,1-dibromocyclopropanes **189** with nitrosyl chloride in the presence of SO_3 occurs in a similar way but with higher selectivity to form aryl-substituted 5-haloisoxazoles.[207, 208] Meanwhile, the reaction of arylcyclopropanes **190** with $(NO)_2[SnCl_6]$ proceeds evidently through another pathway involving the attack of the NO^+ cation on the CHR' group (Scheme 63).[209]

Scheme 63



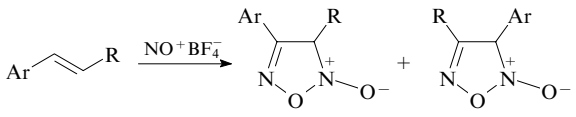
X = Cl, Br; R = H, 3-Br, 3-Cl, 3-NO_2, 4-Br, 4-Cl, 4-NO_2, *etc.*



R = H, OMe; R′ = H, Ph, 4-$MeOC_6H_4$; R″ = H, Me

Aryl-substituted furoxans **191a**,**b** were synthesized by the treatment of styrenes with $NO^+BF_4^-$ (Scheme 64).[210]

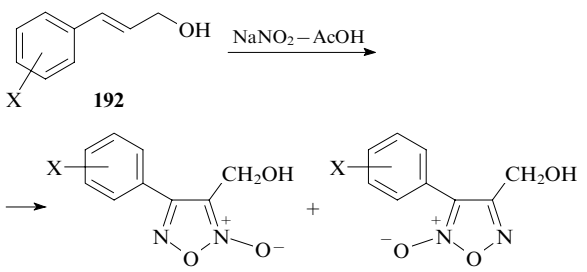
Scheme 64



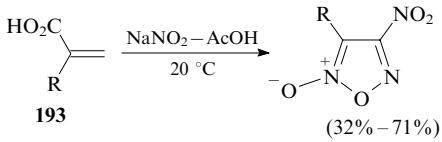
Ar = Ph: R = Me, Ph, n-C_5H_{11}, CH_2OH, CO_2Et;
R = n-C_5H_{11}: Ar = 3-BrC_6H_4, 4-$MeOC_6H_4$, 4-$O_2NC_6H_4$;
Ar = 2-Naph: R = n-C_5H_{11}, Pr^i; Naph is naphthyl

The reaction of the $NaNO_2$–AcOH system with allyl alcohols **192** (see Ref. 211) and acrylic acids **193** proceeds in similar way (Scheme 65).[212]

Scheme 65



X = 3-CF_3, 3-Cl, 3-Br, 4-Me, 4-CF_3, 4-OMe, 4-OH, 4-Cl, 4-Br, *etc.*

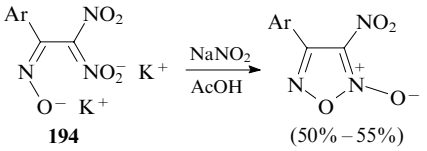


(32%–71%)

R = Me, Pr, Pr^i, Bu, Ph, *etc.*

The treatment of dipotassium salts of 2-aryl-2-hydroxyimino-1,1-dinitroethane **194** with the same nitrosating system gives isomeric 4-aryl-3-nitrofuroxans (Scheme 66).[213]

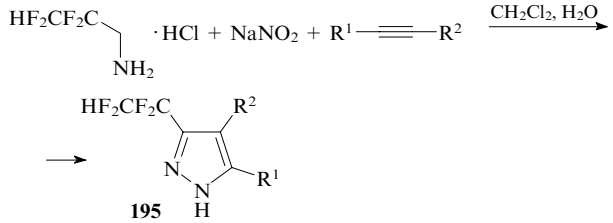
Scheme 66



Ar = Ph, 4-MeO-3,5-$(O_2N)_2C_6H_2$

The three-component reaction involving $H(CF_2)_2CH_2NH_2 \cdot HCl$, $NaNO_2$ and alkynes produces fluorinated pyrazoles **195** in 92%–97% yields (Scheme 67).[214]

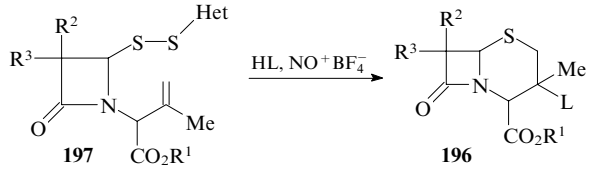
Scheme 67



R^2 = H: R^1 = CO_2Me, CO_2Et, CO_2Pr^i, C(O)Bn, $C(O)(CH_2)_2Ph$, $C(O)C_4H_7$-cyclo, $P(O)Ph_2$; R^1 = R^2 = CO_2Me, CO_2Et

A method for the synthesis of 3-methylcepham-4-carboxylates **196** is based on the cyclization of disulfides **197** with acids in the presence of $NO^+BF_4^-$ (Scheme 68).[215]

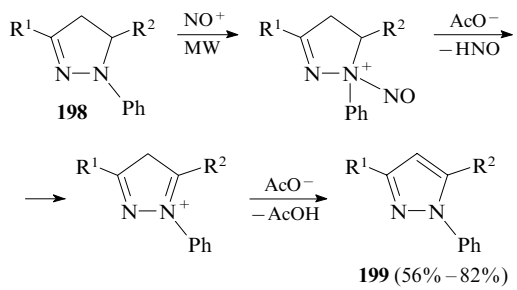
Scheme 68



R^1 = Alk, 4-$MeOC_6H_4CH_2$, 2-$MeOC_6H_4CH_2$, 4-$O_2NC_6H_4CH_2$, Ph_2CH, *etc.*; R^2, R^3 = H, Hal, NH_2, Alk, *etc.*; L = Hal, CF_3SO_3, *etc.*

The microwave (MW)-promoted aromatization of 1,3,5-trisubstituted 4,5-dihydro-1*H*-pyrazoles **198** to pyrazoles **199** was performed using NO^+ generated *in situ* from $NaNO_2$ in acetic acid (Scheme 69).[216]

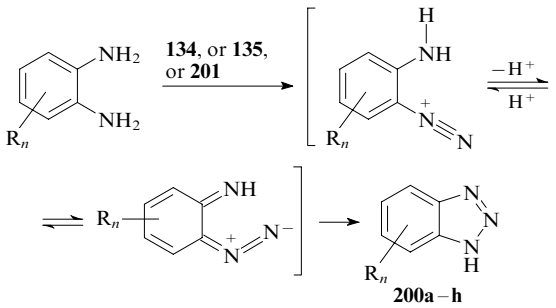
Scheme 69



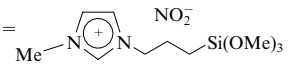
R^1 = Ph, 4-$MeOC_6H_4$, 2-Naph; R^2 = Ph, 2-MeC_6H_4, 4-$MeOC_6H_4$, 4-BrC_6H_4, 2-ClC_6H_4, 3-ClC_6H_4, 4-ClC_6H_4, 4-$O_2NC_6H_4$

Nitrite ionic liquids are efficient reagents for the synthesis of benzotriazole derivatives **200a–h** starting from 1,2-diaminobenzenes. The reaction proceeds under mild and solvent-free conditions and gives products in high yields (Scheme 70, the substituents are given for the starting diamines).[217]

Scheme 70

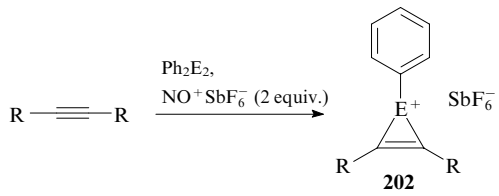


R_n = H (**a**), 4-NO_2 (**b**), 4-Me (**c**), 5-Cl (**d**), 5-NO_2 (**e**), 5,6-Me_2 (**f**), 5,6-Cl_2 (**g**), 5,6-F_2 (**h**);

201 = 

Selenirenium and tellurirenium cations **202** were generated at low temperatures by the reaction of alkynes with the $Ph_2E_2 - 2\,NO^+SbF_6^-$ system (Scheme 71).[218]

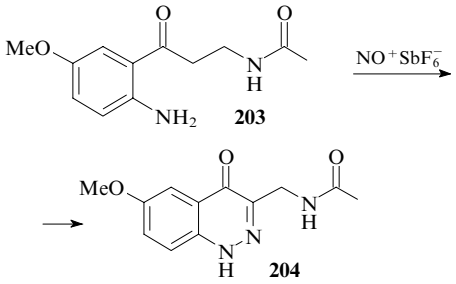
Scheme 71



R = Bu^t, 1-Ad; E = Se, Te; Ad is adamantyl

The treatment of the melatonin metabolite N^1-acetyl-5-methoxykynuramine (**203**) with $NO^+SbF_6^-$ resulted in the formation of 3-acetamidomethyl-6-methoxycinnolin-4-one (**204**) (Scheme 72).[219] Oxidizers (NO^+, $^{\bullet}NO$ and HNO) differ in their capabilities of interacting with this metabolite.

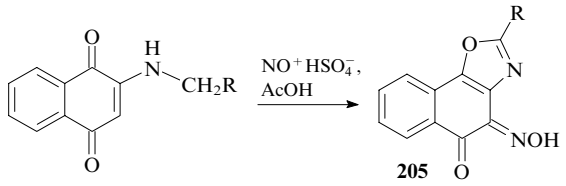
Scheme 72



2-Alkylnaphtho[2,1-*d*][1,3]oxazole-4,5-dione 4-oximes **205** were synthesized in 62%–66% yields by the reaction of 2-alkylamino-1,4-naphthoquinones with nitrosylsulfuric acid (Scheme 73).[220]

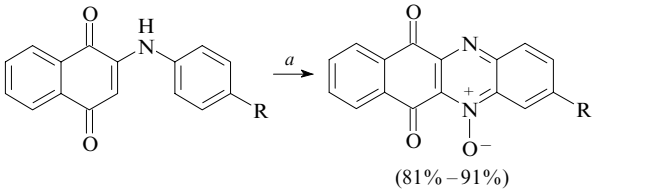
The replacement of the alkyl group in these substrates by the aryl or benzyl moiety causes a change in the reaction pathway (Scheme 74).[221,222]

Scheme 73

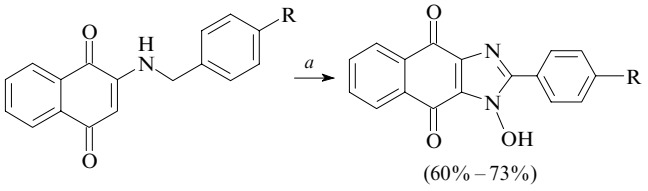


R = Me, Et, Pr^n, Pr^i

Scheme 74



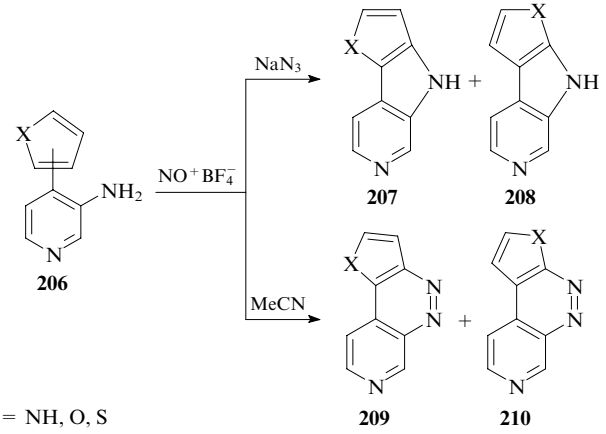
R = H, Me, F, Cl; (*a*) $NO^+HSO_4^-$, AcOH



R = H, Me, Cl; (*a*) $HNO_3-H_2SO_4$, AcOH

The diazotization of aromatic amines **206** with $NO^+BF_4^-$ followed by cyclization affords tricyclic compounds **207**–**210** in low yields (Scheme 75).[223, 224]

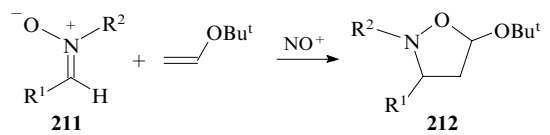
Scheme 75



X = NH, O, S

The nitrosonium cation is an efficient catalyst for [3 + 2]-cycloaddition involving nitrones **211** and vinyl ethers, in particular, *tert*-butyl vinyl ether, giving isoxazolidines **212** (Scheme 76).[225]

Scheme 76

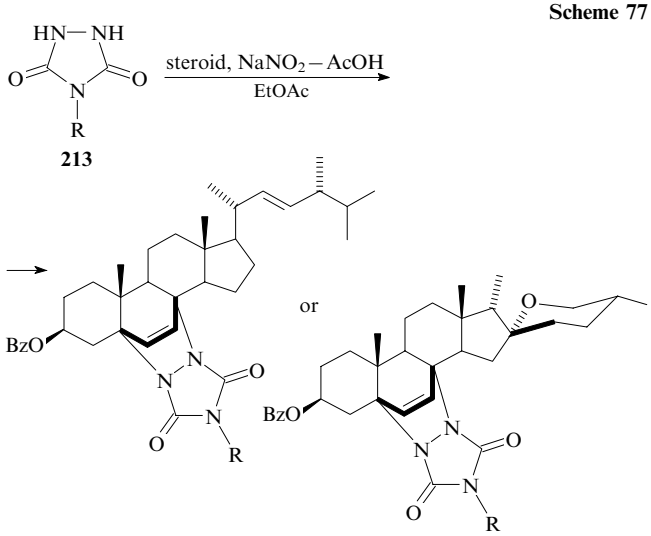


R^1 = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-ClC_6H_4, 4-FC_6H_4, 4-$MeO_2CC_6H_4$, 1-Naph, *etc.*; R^2 = Ph, 4-ClC_6H_4, 4-$MeOC_6H_4$

Fernández-Herrera *et al.*[226] proposed a selective version of the Diels–Alder reaction of steroids with urazoles **213** with the participation of nitrosonium ion generated *in situ* by the $NaNO_2-AcOH$ system (Scheme 77). This method can be applied to protect the diene system of the steroid.

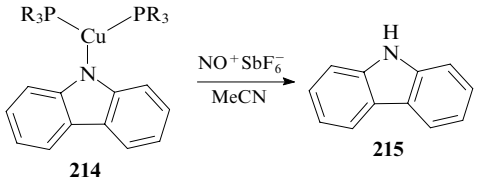
The oxidation of copper complex **214** with $NO^+SbF_6^-$ in MeCN gives carbazole (**215**) in 60% yield (Scheme 78).[227]

Scheme 77



R = Ph, $C_6H_4NO_2$-4, N=CHPh, $N=CHC_6H_4OMe$-4

Scheme 78



R = 3-MeC_6H_4

Therefore, nitrosonium salts serve as both reactants and catalysts in the synthesis of various heterocyclic compounds.

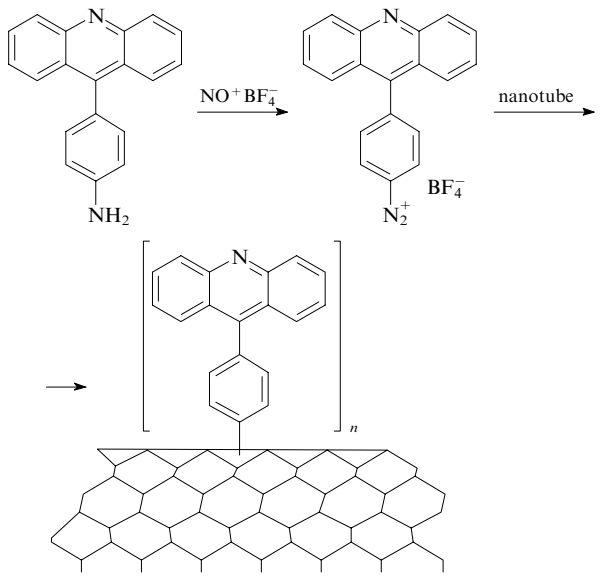
VII. Use of nitrosonium salts for the preparation of modern materials

Nitrosonium salts are widely used for the fabrication of luminescent materials,[228, 229] solar cells,[230–234] electroconductive polymers,[235–237] as well as for modification of carbon nanotubes[238, 239] and other materials.[240–246] A strategy was developed for surface functionalization of nanocrystals (metal oxides, metals, semiconductors and dielectrics) based on the use of the $NO^+BF_4^-$ salt for the treatment of organic ligands attached to the nanocrystal surface.[247] During the oxidation of ruthenium nanoparticles protected by octynyl moieties with this salt, a long-wavelength band centred around 1687 nm started to emerge in the electronic absorption spectrum, the intensity and shape of the band being dependent on the amount of the salt added.[248] The $NO^+BF_4^-$ salt was proposed as a dopant for an electron-donating layer composed of trimethine cyanine dye in solar cells.[249] This doping procedure results in an increase in the conductivity of the electron-donating layer. The $NO^+PF_6^-$ or $NO^+BF_4^-$ salts were employed to fabricate thermoelectric films based on poly{2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-*b*]thiophene}[250] and in the synthesis of nanoparticles doped with lanthanide ions.[251] These nanoparticles are of interest as materials for solar cells, 3D

displays and visualization of biomolecules. The oxidation of dimagnesium (4,4′-dioxidobiphenyl-3,3′-dicarboxylate) [Mg_2(dobpdc)] with $NO^+PF_6^-$ was used as a model process to investigate the porous metal-organic framework Fe(dobpdc)$_2$ as a material for a ion-battery cathode.[252] In a patent,[253] the $NO^+PF_6^-$ salt was employed as an oxidizing agent introduced into a electroconductive polymer layer in organic photoelectric cells.

The functionalization of nanomaterials by means of diazotization with the participation of nitrosonium salts is a widely used approach.[254–256] It is based on high reactivity of aryl cations that are formed *via* decomposition of diazonium salts of arylamines. A method for attaching organic moieties to the surface of semiconductor nanostructures by treating substituted anilines with $NO^+BF_4^-$ has been patented.[257] 4-(2,2′:6′,2″-Terpyridin-4′-yl)benzenediazonium tetrafluoroborate, which was synthesized by the reaction of $NO^+BF_4^-$ with the appropriate amine, was employed to modify the surfaces of carbon nanotubes and other materials.[258] The attachment of terpyridine moieties to the surface of materials provides surface functionalization with metal complexes, which holds promise for the construction of optical-electronic devices. A method was developed for the direct grafting of diazonium calixarenes, which were synthesized by treating calixarene amines with $NO^+BF_4^-$, onto the surface of composite materials, nanoparticles, polymers and nanotubes.[259] Nanotubes **216** covalently modified with 9-phenylacridine were prepared by the reaction of the appropriate diazo compound with the nanotube. The fluorescence spectrum of such nanotubes is shifted to longer wavelengths with respect to the spectrum of individual 9-phenylacridine (Scheme 79).[260] In the authors' opinion, this is the first example of the formation of an exciplex between a nanotube and an aromatic molecule.

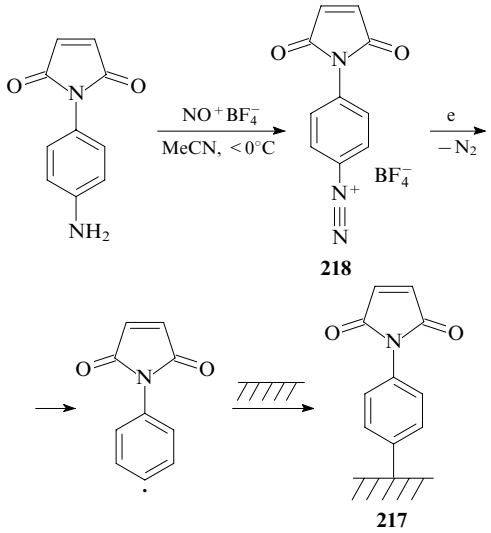
Scheme 79



216

Multifunctional thin films on a gold substrate were prepared by consecutive electrodeposition of diazonium salts, which were produced by the reaction of $NO^+BF_4^-$ with 4-nitroaniline and 4-(4,4,5,5-tetramethyl-2-*p*-tolyl-1,3,2-dioxaborolan-2-yl)phenylamine.[261] A similar approach was applied to fabricate surfaces functionalized with maleimide moieties (structure **217**) by means of electrochemical reduction of aryl diazonium salt **218** (Scheme 80).[262]

Scheme 80

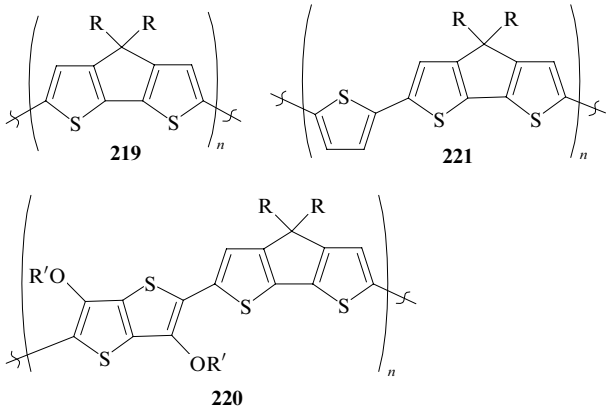


218

217

The salts NO^+X^- [X = BF_4, PF_6, HSO_4, FSO_3, CF_3SO_3, $(CF_3SO_2)_2N$] were proposed as additives for improving the performance characteristics of electrochemical cells and batteries.[263] 4-Dodecyloxybenzenediazonium tetrafluoroborate generated by the reaction of $NO^+BF_4^-$ with the appropriate amine reacts with metallic single-walled carbon nanotubes under kinetic control.[264] The $NO^+BF_4^-$ salt was employed to improve the semiconducting properties of carbon nanotubes.[265] The reaction of oxetane derivatives with $NO^+SbF_6^-$ is accompanied by polymerization giving electroconductive films.[266] The treatment of polymer films, prepared from polymers **219**–**221**, with nitrosonium tetrafluoroborate results in the oxidation and the appearance of bands at >920 nm in electronic absorption spectra.[267] These materials are of interest as active layers in microelectronics.

Structures 219–221



219 **221**

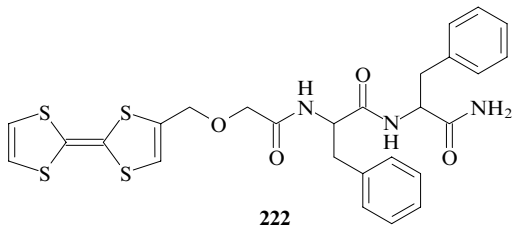
220

R, R′ = n-C_8H_{17}, $(CH_2)_2CH(Me)(CH_2)_3Pr^i$

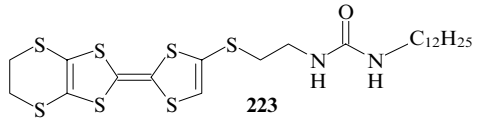
A poly(3-hexylthiophene) film oxidized with $NO^+PF_6^-$ can serve as a highly sensitive gas chemosensor for ammonia.[268] The $NO^+PF_6^-$ salt was employed as a dopant for a polythiophene gas sensor.[269] The photoconduction in polymer films based on thiophene derivatives can be enhanced by their doping with $NO^+BF_4^-$.[270] This salt was also employed as a dopant for the alternating copolymer poly{2,7-(9,9-dioctylfluorene)-*alt*-5,5-(4′,7′-bis(2-thienyl)-2′,1′,3′-benzothiadiazole)}.[271] Electroconductive gels based

on tetrathiafulvalene derivatives **222** (Ref. 272) or **223** (Ref. 273) were prepared using the $NO^+PF_6^-$ salt.

Structures 222, 223



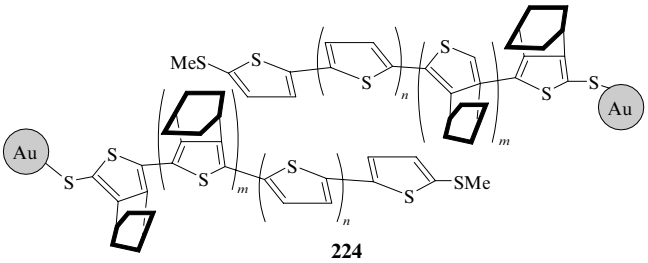
222



223

The treatment of tetrathiapentalene derivatives with nitrosonium salts gives a polymer with an electrical conductivity of 10^{-3} to 10^{-1} S cm^{-1} (Ref. 274). After chemical doping using a solution of $NO^+BF_4^-$ in MeCN, the conductivity of poly(hexylthiophene) nanofibres reached 0.25 S cm^{-1} (Ref. 275). Tateno *et al.*[276] prepared gold nanoparticles protected by ter- or quaterthiophene, which was partially annulated with bicyclo[2.2.2]octene units and contained methylthio anchoring groups at the termini. The electric conductivity of films composed of these nanoparticles depends on the number of thiophene moieties and varies from 10^{-3} to $<10^{-6}$ S cm^{-1}. Bicyclooctene units were introduced in order to suppress π–π interactions between oligothiophenes attached to the same Au nanoparticle and promote interaction between oligothiophenes on neighbouring particles (Structure **224**).

Structure 224

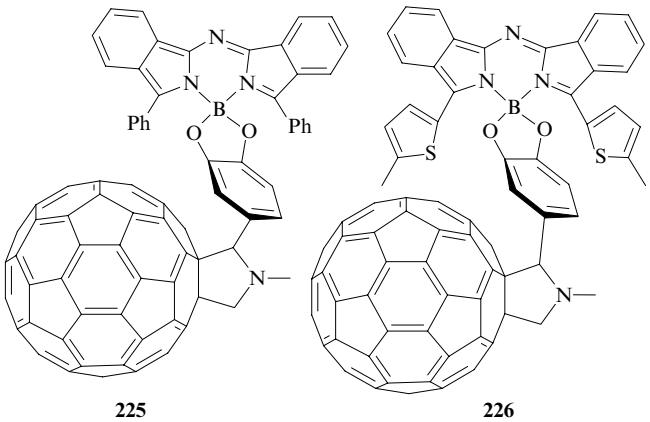


224

m, *n* = 0, 1

Electrodes modified with a film using Nafion, Nafion-$\{Ru_2^{III}(\mu\text{-OH})\}$, selectively reduce NO^+, apparently, *via* a key reaction of the mixed valence intermediate $\{Ru^{II}Ru^{III}(\mu\text{-OH})\}$ with HNO_2, these films being stable at physiological pH values.[277] The spectral identification of oxidation products of the compounds BADP-C60 (**225**) and TADP-C60 (**226**) during photochemical charge separation in donor-acceptor pairs was accomplished using nitrosonium tetrafluoroborate as an oxidizing agent.[278]

Structures 225, 226



225 **226**

VIII. Nitrosonium cation in biochemical reactions

The nitrosonium cation represents an oxidized form of nitrogen(II) oxide that plays an important role in living organisms.[279,280] In biological systems, the NO^+ cation is produced through the oxidation of an NO molecule with molecular oxygen, superoxide anion or transition metal compounds.[5,6,281] The autooxidation of NO in the body results in the generation of an N_2O_3 molecule, which gives the nitrosonium cation.[282–284] The NO^+ cation generated by oxidation reacts with nucleophilic centres of ROH, RR′NH and RSH molecules, including protein thiol groups,[285] the bacteriostatic effect of NO^+ as a component of nitrosothiols is 100-fold stronger compared to NO.[286] The nitrosonium cation can react with biological thiols, such as glutathione or cysteine, to form S-nitroso compounds, which are quite stable and can extend the effects of nitric oxide beyond the site of its generation.[287] In the free state, the NO^+ cation can exist in aqueous solutions only at a pH level lower than physiological pH values.[288] In aqueous solutions, NO^+ rapidly reacts with water to give HNO_2 and its dissociated form, $H^+ + NO_2^-$. At physiological pH values (~7.0–7.4), the $NO^+ : NO_2^-$ ratio in equilibrium is $\sim 10^{-17}$, and the lifetime of the NO^+ cation in water is very short ($\tau_{1/2} = 10^{-10}$ s) because of the rapid interaction with water [reaction (2)].[289,290]

$$NO_2^- + 2H^+ \rightleftharpoons NO^+ + H_2O \qquad (2)$$

The *ab initio* molecular dynamics simulation gave even a shorter lifetime for the NO^+ cation in water ($\sim 4 \times 10^{-13}$ s),[291] although this value is highly unlikely since it is close to the lifetime of the transition state. Nitrosothiols (formally NO^+ cation + thiolate anion) are quite stable at physiological pH values and are functional equivalents of NO^+.[288] The S-nitrosation of glutathione occurs after the initial step of the reaction between NO and oxygen, the hydrophobic protein environment apparently playing an insignificant role in the formation of S-nitrosothiols.[292] The nitrosonium cation is most likely involved in the reaction of glutathione with dinitrosyl iron complexes in the presence of atmospheric oxygen.[293] Dinitrosyl iron complexes with thiol-containing ligands can serve as donors of NO^+ in different cells and tissues of the body.[294] The nitrosonium cation is a good ligand for a haem iron atom and can be efficiently transferred from nitrosothiols.[295] The NO^+ cation can be produced in cells from nitrosyl complexes of metals, for example, from sodium nitroprusside.[296] Due to the presence of ascorbates, the nitrosonium cation is rapidly converted into an NO molecule. Metalloproteins, such as transferrin and ceruloplasmin, interact with nitric oxide and form metal nitrosyl complexes, which can serve as a NO^+ source.[297] It is assumed that the nitrosonium cation, which is produced *via* the oxidation of nitric oxide by ceruloplasmin, can replace a hydrogen atom in thiol groups of albumin and glutathione or react with water to form nitrite. Although the albumin and glutathione concentrations in the blood plasma are rather high, the authors

hypothesized that the reaction of nitrosonium cation with water is the dominating process.[298] The NO^+ cation can be stabilized through coordination to metals.[299, 300] One of specific features of a series of metal nitrosyl complexes is the versatile character of the NO ligand. Thus, the conversion of $M \cdot NO^-$ into $M \cdot NO^+$ may be accompanied by a change in the oxidation state of the metal atom. For instance, *Escherichia coli* superoxide dismutase (SOD) — a manganese-containing enzyme — catalyzes the disproportionation of NO to give NO^+ and NO^- [reactions (3) and (4)].[301]

$$Mn^{III}SOD + NO \longrightarrow Mn^{II}SOD\cdots NO^+ \quad (3)$$

$$Mn^{II}SOD + NO \longrightarrow Mn^{III}SOD\cdots NO^- \quad (4)$$

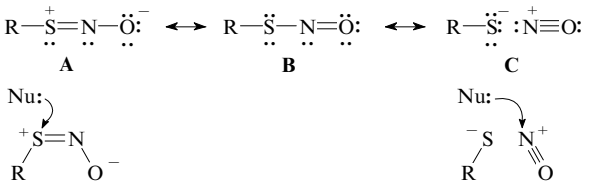
Metal nitrosyl complexes can behave as electrophiles and react with such nucleophiles as RSH, resulting in the NO^+ cation transfer [reaction (5)].[302–304]

$$L_xM-NO + RSH \longrightarrow RS-NO + L_xM + H^+ \quad (5)$$

Copper and iron ions can catalyze the decomposition of nitrosothiols to form NO^+, NO and RSSR or RS^-.[305]

The delivery of NO into cells may involve the transnitrosation reaction, in which nitrosothiols act as NO^+ donors.[306] Nitrosothiols are more stable than the NO molecule, which makes them potential NO reservoirs.[307] A nitrosothiol molecule can be represented by the canonical resonance structures **A**–**C** reflecting the interaction of nucleophiles at either the sulfur or nitrogen atom (Scheme 81).[308, 309]

Scheme 81



The dual nature of the SNO group is manifested in viriations in the SN bond length. This bond is nearly a double bond in the structure **A** and is unusually long in the structure **C**. The structure **A** is favourable for the nucleophilic attack on the S atom bearing a positive charge, whereas the structure **C**, which formally incudes the nitrosonium cation, implies the nucleophilic attack on the nitrogen atom. The computer simulation demonstrated that the properties of nitrosothiols can be dramatically altered by an external electric field.[308]

The S-nitrosation is related to the signal transduction mechanism in cells. The conversion of nitrogen oxide ($NO^{\bullet}$) into nitrosonium cation may have important consequences for signal transduction and physiological responses.[310] Stereoselective effects of endogenous nitrosothiols are manifested in physiological redox signal transduction. For instance, high stereospecificity of S-nitrosothiols in biological systems is apparently associated with their ability to support NO^+ transfer *in vivo* within sterically restricted signalling regions by protecting redox-responsive cysteine residues in regulatory proteins.[311] The NO^+ cation rather than the NO molecule causes airway smooth muscle relaxation *via* cyclic guanosine monophosphate-independent release of Ca^{2+} ions.[312] It is assumed that L-arginine modifies the NO molecule into redox-active NO^+, resulting in rat renal artery relaxation.[313] Nitrosothiols are involved in transnitrosation, *i.e.*, in the transfer of the NO^+ cation to proteins.[314–316] The transfer of the NO^+ cation from mitochondria-targeted S-nitrosothiols (MitoSNO1) to protein thiol groups changes the function of the proteins, which can be used to regenerate the bloodstream after the ischemic event.[317] Nitrosothiols may have a protective function for thiol groups of enzymes, thus preventing irreversible oxidative damage of the latter.[318] *N*-Nitrosomelatonin can operate as a source of nitric oxide. It can transfer the nitrosonium cation to hydroxy-containing compounds (vitamins C and E, benzenediols, serotonin) to form melatonin and NO.[319]

Dinitrosyl iron complexes with thiolate ligands and S-nitrosothiols inhibit catalase, neutral nitric oxide rather than the NO^+ cation being responsible for inactivation of the enzyme.[320] Dinitrosyl iron complexes exhibit antitumour activity[321–323] and inhibit platelet aggregation.[324] The resistance of cancer cells to apoptosis is regulated by NO^+-induced S-nitrosylation of key enzymes.[325] Haemoprotein nitrosyl complexes are quite stable and can be involved in redox reactions to form the NO^+ cation [reaction (6)].[304, 316]

$$\text{haem-Fe}^{3+} + NO \rightleftharpoons \text{haem-Fe}^{3+}-NO \longrightarrow \text{haem-Fe}^{2+} + NO^+ \quad (6)$$

The nitrosonium cation can be generated by the reduction of transition metal cations (Fe^{3+} or Cu^{2+}) with an NO molecule, thus affecting the signal transduction in cells.[326] The oxidation of NO gives NO^+ followed by its removal from the signalling system. The effect of NO removal may be significant in pathological conditions, such as heart failure or diabetes, where a low NO concentration can lead to the development of the diseases. Laser radiation accelerates the decomposition of cytochrome *c* nitrosyl complexes (cyt $c)^{3+}-NO$ to form, most likely, (cyt $c)^{2+}$ and NO^+ (Ref. 305). It was demonstrated that the NO^+ cation is involved in nitrosative stress.[327, 328] In the postischemic period, excess of NO interacts with haem iron and pairs of thiol groups to produce a dinitrosyl iron complex. These complexes with thiol-containing moieties can act as NO^+ donors in different cells and tissues of the body, resulting in the formation of N- and S-nitrosothiols, the shift of the thiol–disulfide equilibrium and the development of nitrosative stress.[324] In the presence of NO at a higher concentration, toxic oxide N_2O_3 is formed. The latter, as a source of NO^+, acts as a nitrosating agent and reacts with aliphatic and aromatic amines to give *N*-nitroamines. Their conversion products are involved in nucleic acid alkylation and purine deamination. The reaction of N_2O_3 with cysteine yields *S*-nitrosocysteine and the reaction with glutathione gives *S*-nitrosoglutathione.[329]

For many years, nitrates have been used as food additives.[330] Although a nitrate ion is not toxic by itself, its reduction to the nitrite ion can give rise to N_2O_3, which, in turn, generates the nitrosonium cation. This cation reacts with secondary amines to form nitrosamines, many of which are carcinogenic even at very low doses.

The above data provide evidence that the NO^+ cation plays an important role in biochemical reactions. Unfortunately, the detailed mechanism of the involvement of the nitrosonium cation in these reactions is poorly understood, which is attributable to the complexity and diversity of biochemical processes. In this context, noteworthy are reviews by Nakamura and Lipton,[331, 332] who discussed the possible involvement of the NO^+ cation in S-nitrosylation

of proteins. In the schemes presented in these reviews, the NO^+ cation is enclosed in brackets, thus indicating that the detailed mechanism of its involvement is not established. Living organisms contain plenty of molecules (proteins, enzymes, DNA and so on) with nucleophilic O-, N-, S- and C-centres and can evidently form cationic nitrosonium complexes. The lifetime of these complexes may be much longer than that of the free NO^+ cation. These complexes can be involved in nitrosonium cation transfer. The above data on the dynamics of nitrosonium complexes demonstrate that this transfer can proceed at a high rate. Unfortunately, experimental data on the direct observation of nitrosonium complexes of biomolecules by spectroscopic methods are lacking.

IX. Conclusion

The data presented in this review demonstrate diverse functions of the nitrosonium cation in chemical and biochemical reactions. Methods for nitrosation and diazaotization of different classes of organic compounds are being extensively developed, and there is a revival of classical reactions in organic chemistry. The nitrosonium cation is a strong oxidizing agent. Its salts are widely used for the preparation of radical cations of organic compounds. The reduction of the NO^+ cation produces nitric oxide gas, thus allowing the synthesis of these salts in the pure state. Zeolite catalysts hold promise for the selective catalytic reduction of nitrogen oxides with hydrocarbons. This is of great importance for environmental protection taking into account the wide application of motor fuels, combustion of which releases NO_x gases. The NO^+ cation is assumed to be involved in reduction of these gases with alkanes on zeolites. However, the mechanism of reduction is poorly understood, and further detailed investigations are required. The development of methods for the fixation of N_xO_y gases to form nitrosonium complexes of calixarenes and nanotubes is of interest for the analysis of these gases in the atmosphere. This issue is important in tackling environmental challenges. Nitrosonium salts are of considerable interest as reagents in the synthesis of various heterocyclic compounds. In this respect, nitrite ionic liquids show considerable promise because they make it possible to synthesize N,O-heterocycles under mild conditions. Nitrosonium salts are widely used for the fabrication of luminescent materials, electroconductive polymers for the manufacture of solar cells, as well as for modification of nanotubes and other materials. Investigations of the structures and properties of clusters that are formed during modification of metals and nanotubes by means of diazotization give insight into the functioning of semiconductors, chemosensors and other nanomaterials and a key to the prediction of their chemical and physical properties and also provide the approach to their practical application in electronics, medicine and other fields.

Investigations of the mechanism of interaction between the NO^+ cation and DNA bases are important for the understanding of genetic modification processes. The resistance of cancer cells to apoptosis is regulated by NO^+-induced S-nitrosylation of key enzymes. Understanding of this process is of great importance in the fight against cancer. The mechanisms of involvement of nitrosonium cation in biochemical processes are poorly known because of the complexity of the objects of investigation and the short lifetime of the NO^+ cation under physiological conditions. The use of quantum chemical methods for the simulation of biochemical reactions and investigation of the structures and properties of nitrosonium complexes with biomolecules holds some promise.

The present review makes an attempt to hold together all the published information on the role of the nitrosonium cation in organic and biochemical reactions in view of relevant recent progress in this field of research, including the practical application of nitrosonium salts in the synthesis of heterocyclic compounds, the construction of nanomaterials and the employment of the NO^+ cation as an oxidizing agent for organic compounds and as a catalyst for industrially important reactions. The knowledge of the structures and properties of nitrosonium complexes as intermediates and sources of NO^+ will extend the theoretical understanding of the chemical and biochemical processes involving the nitrosonium cation.

This review has been written with the financial support of the Division of Chemistry and Materials Science of the Russian Academy of Sciences (Project 5.1.4).

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