

Reactions of alkenes with nitrogen oxides and other nitrosating and nitrating reagents

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Abstract. Reactions of alkenes with nitrogen oxides and other nitrosating and nitrating reagents are considered. The bibliography includes 134 references.

I. Introduction

Reactions of alkenes with nitrogen oxides and other nitrosating and nitrating reagents have attracted attention during the entire history of contemporary organic chemistry. The fundamental studies carried out in this area are of independent significance and have contributed considerably to the arsenal of organic synthesis by providing new preparative methods and accessible highly reactive synthetic blocks.

In this review, we consider the transformations of alkenes in reactions with NO, NO₂, their synthetic equivalents and sources of NO⁺, NO₂⁺ and NO₂⁻ ions. Aside from differences originating from the specific nature of each of these reagents, their reactions with alkenes have certain common features which manifest themselves in the similarity of the intermediates and products formed. Particular attention is paid to reactions which result in aliphatic and alicyclic nitro compounds, since the uses of these compounds in organic synthesis are the most diverse (see., *e.g.*, the reviews^{1–8}).

The transformations discussed here have been reported in the last 10–15 years. Earlier examples can be found in other reviews.^{9–12} In particular, reactions of alkenes with N₂O₃, N₂O₅ and HNO₃ have been considered in detail in those reviews; however, there have been few publications on these reagents recently,^{13,14} since, as a rule, their reactions have only limited application in preparative synthesis. One should note, however, a recently developed original solid-phase method for the synthesis of 2-arylnitroethenes from styrenes under microwave radiation in the presence of Fe(NO₃)₃·9H₂O or an NH₄NO₃–clay system.¹⁵

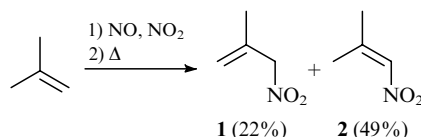
Likewise, we do not consider reactions of alkenes with NOCl discussed in detail previously,¹⁶ since this reagent has rarely been used for alkene functionalisation in recent years.¹⁷

II. Reactions of alkenes with NO

Although the NO molecule has an unpaired electron, it is characterised by its low activity toward potential acceptors of free radicals.¹⁸

At present, evidence is available that NO cannot add directly to alkenes. It was reported back in 1957 that meticulously purified NO can be kept in contact with liquid alkenes for a few days without noticeable interactions.¹⁹ It was reported later that pure NO did not react with functionally substituted alkenes (allyl benzyl ether, acetylcyclohexene) or with 1,4-diphenylbuta-1,3-diene.²⁰ It was also found that alkenes with electron-donating substituents at a double bond (butyl vinyl ether and silyloxycyclohexene) undergo changes in the presence of NO but no nitrogen-containing compounds are formed.

On the other hand, there are rather many examples where nitrogen-containing products are obtained in NO–alkene systems. In the study mentioned above,¹⁹ isobutene reacted with NO (from a gas cylinder) containing an admixture of NO₂ to give nitroisobutene **1** and a labile compound with unknown structure, which decomposed during high-vacuum distillation to give nitroalkene **2**.

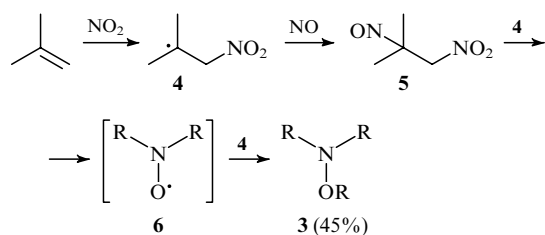


Brown¹⁹ emphasised that traces of NO₂ in NO are a prerequisite for the reaction. It was assumed that it is NO₂ that triggers the free radical process which continuously regenerates NO₂. This hypothesis was confirmed by the well-known ability of free radicals (including alkyl radicals) to convert NO into NO₂.²¹ According to more accurate data reported later,²² the reaction in the NO–isobutene system yields a very labile hydroxylamine **3** as the main product. The latter is presumably formed as a result of successive reaction of NO with three nitro-*tert*-butyl radicals **4** (which result from the addition of NO₂ present in NO to the alkene) *via* the nitro nitroso compound **5** and the iminoxyl radical **6**.

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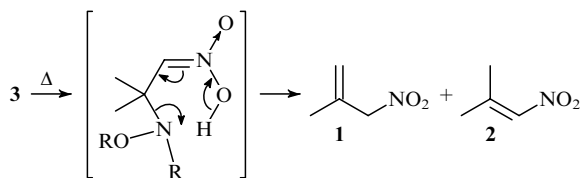
Uspekhi Khimii 72 (4) 363–378 (2003); translated by S S Veselyi



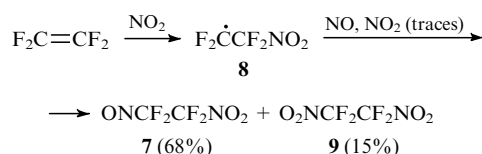
R = CMe₂CH₂NO₂.

It should be noted that the radical **6** was detected in an ESR study of this reaction.²³ In addition, nitro-*tert*-butyl radicals **4** were also identified. It was noted that the addition of oxygen to the reaction medium accelerated the process considerably; this confirms the activating role of NO₂, the concentration of which in the reaction mixture increases due to the oxidation of NO.

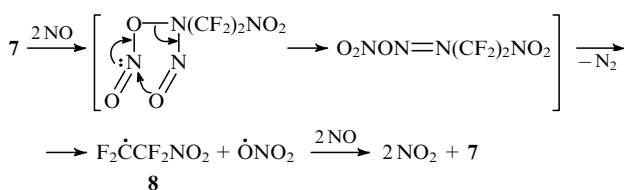
On moderate heating, hydroxylamine **3** gives a mixture of nitrosobutenes **1** and **2** in the ratio 1 : 4 and in an overall yield of 85%. It is assumed that the reaction occurs *via* a six-membered transition state.²²



The relatively stable 1-nitro-2-nitroso-1,1,2,2-tetrafluoroethane **7**, which is akin to the intermediate **5** postulated by Phillips and Coyne,²² is the major product formed in the NO–tetrafluoroethylene system.²⁴



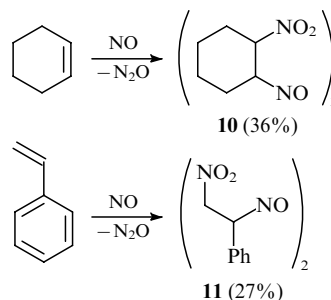
The suggested reaction mechanism also involves initiation of the chain process by NO₂ radicals, which are more reactive than NO. The resulting radical **8** is subsequently recombined with NO to give the nitro nitroso compound **7**. This mechanism is confirmed by the fact that no 1,2-dinitrosotetrafluoroethylene was present in the reaction products; the presence of the latter would have meant that the process was initiated by direct addition of NO to the alkene. The authors noted that the reaction was accelerated considerably on addition of NO₂ to the reaction mixture and suggested the possible ways of its formation. In particular, the reaction of perfluoronitronitrosoethane **7** with an excess of NO may give two NO₂ molecules per molecule of the nitroso compound.



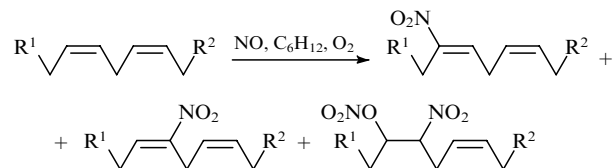
When the concentrations of NO₂ and NO become comparable, the recombination of NO₂ with the radical **8**, which terminates the chain process and gives the side dinitro compound **9**, acquires a progressively significant role.

The formation of NO₂ is also possible as a result of disproportionation $3\text{NO} \rightarrow \text{NO}_2 + \text{N}_2\text{O}$, which is favoured by an increase in pressure.

For example, it was found²⁵ that thoroughly purified NO reacted at a noticeable rate with cyclohexene or styrene only at pressures above 5 atm; a GC/MS study of the gaseous reaction products revealed the presence of N₂O. At 7 atm, the corresponding dimeric nitro nitroso compounds **10** and **11** were isolated as the main reaction products; their structures were established by X-ray diffraction analysis. However, when this reaction was carried out with raw NO under atmospheric pressure, analysis of the gas mixture also showed that a small amount of N₂O was present.²⁶



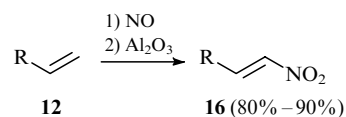
The fact that the presence of NO₂ plays a key role in the reaction of NO with alkenes is also confirmed by results of other studies^{27,28} where linoleic and arachidonic acids and their esters were used as substrates (as models of unsaturated lipids). The air equilibrated reactions were carried out in cyclohexane or benzene. Complex product mixtures were obtained; based on spectroscopic data, nitroalkenes and nitro nitrates were the main components of these mixtures. It was noted that this process was virtually not observed if the reaction mixture did not contact air.



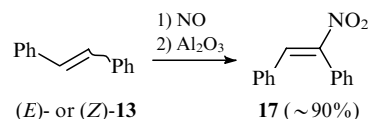
R¹ = (CH₂)₃Me, R² = (CH₂)₆CO₂Et; R¹ = (CH₂)₆CO₂Et, R² = (CH₂)₃Me.

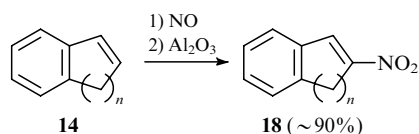
It is evident from the examples described above that reactions in alkene–NO systems are not straightforward; as a rule, they give mixtures of products. What is more, their results depend on the purity of nitrogen oxide used. However, studies of the nature of processes in this system have made it possible to develop an efficient method for converting mono- and disubstituted alkenes of the type **12–15** into conjugated nitro derivatives.^{29–31}

According to the standard procedure, a solution of an alkene in dichloroethane is stirred under NO, then acidic alumina is added to the reaction mixture, which is refluxed for a short time. The yields of the corresponding vinylnitro compounds **16–19** reach 90%. It was found later that treatment with Al₂O₃ can be excluded by performing the reaction in the presence of H-zeolites.³²

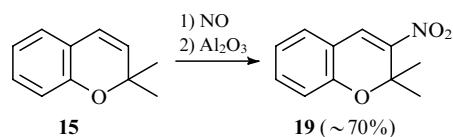


R = Alk, Ar, (CH₂)₃X; X = CH₂Ac, OSiMe₂Bu^t, OAlk.





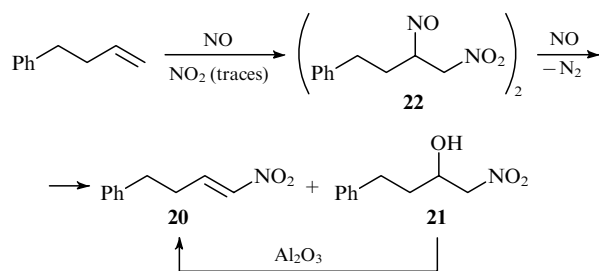
$n = 1, 2.$



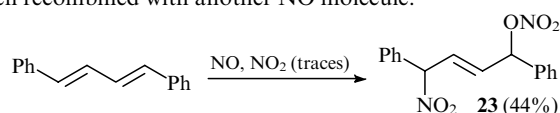
A detailed study of the characteristic features of this process using 4-phenylbut-1-ene as an example made it possible to reveal certain regularities. It was found that complete conversion of the alkene requires four equivalents of NO. A mixture (~4 : 1) of the vinylnitro compound **20** and the nitro alcohol **21** is formed initially (Al₂O₃ is used for the dehydration of the latter). Analysis of the reaction products revealed its stoichiometry:



Using a lesser amount of NO, Hata *et al.*³⁰ isolated the dimer of an intermediate nitro nitroso compound **22**, which reacts with NO to give nitroalkene **20** with liberation of one equivalent of N₂.

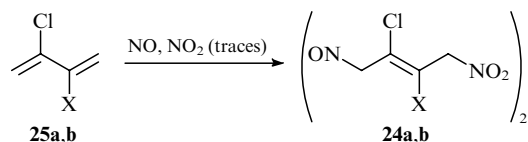


As noted above, there is evidence that thoroughly purified NO does not react with 1,4-diphenylbuta-1,3-diene.²⁰ This observation contradicts earlier data,³³ according to which the reaction of NO with 1,4-diphenylbuta-1,3-diene gives the nitro nitrate **23**. However, it was assumed that the chain radical process is initiated by direct addition of NO to the diene to give an allyl radical, which then recombined with another NO molecule.

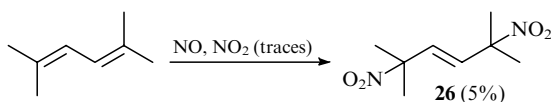


The accumulation of NO₂, which gives rise to the dinitro derivative **23**, is rationalised as follows: the nitroso compound formed initially can sequentially add two NO molecules to give the [•]ONO₂ radical. The latter reacts with NO to give two molecules of nitrogen dioxide, which competes with NO as the initiator of the radical chain process.

The suggested mechanism also offers an explanation of the formation of dimeric nitroso compound **24a,b** from 2-chloro-(**25a**) and 2,3-dichlorobuta-1,3-diene (**25b**) under similar conditions. In addition, this reaction gives polymers which, according to IR spectroscopic data, contain NO₂ and ONO₂ functional groups. Complete conversion of 2,5-dimethylhexa-2,4-diene afforded a quite stable dinitro compound **26** and a polymeric product.³³



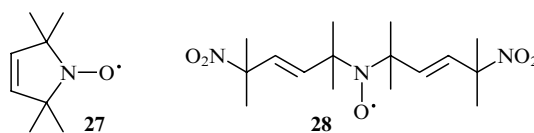
X = H (**a**, 15%), Cl (**b**, 40%).



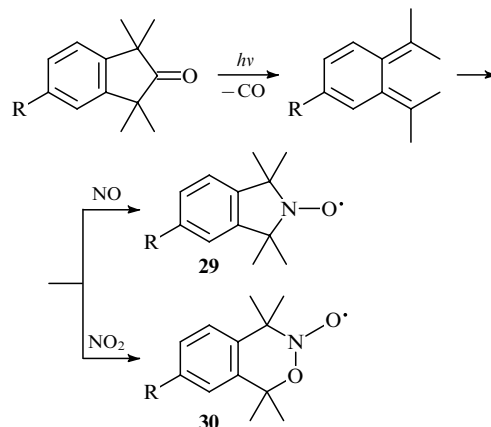
It should be noted that the reactions of NO with di(poly)enes are currently considered as a promising way to solve the problem of *in vivo* monitoring of this biologically important molecule³⁴ using the ESR method. In particular, it was found³⁵ that absorption of NO with such conjugated polyenes as vitamins A and D₃, as well as β-carotene, results in the appearance of distinct signals of iminoxyl radicals in ESR spectra. It was noted that NO₂ addition products could not be detected in the reaction mixtures.

Treatment of 2,5-dimethylhexa-2,4-diene with nitrogen(II) oxide also resulted in the appearance, in the ESR spectrum, of signals of an iminoxyl radical,^{36,37} which is assumed to have the cyclic structure **27**. However, attempts to isolate it failed.³⁸

However, as was shown later,²⁰ the signals in the ESR spectrum recorded in this case are due to the presence of the iminoxyl radical **28**, which is formed upon initiation of the process by nitrogen(IV) oxide present in NO as an admixture, and the formation of a nitroallyl radical intermediate.



The idea of using dienes as efficient NO traps in biological objects was implemented using *o*-quinodimethanes, which can be obtained by photolysis of the corresponding indanones.^{39,40}

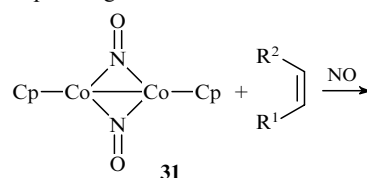


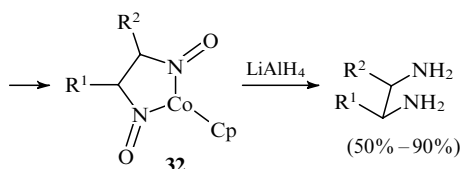
R = CO₂H, Et₃N⁺CH₂.

Stable iminoxyl radicals **29** formed upon reactions of quinodimethanes with NO can be reliably detected by ESR. Hydrophilic properties required for the use of these compounds in biological systems are provided by incorporation of substituents (R = CO₂H, Et₃N⁺CH₂). It is of interest that the ESR spectra of reaction mixtures also contain traces of radicals **30** resulting from the addition of NO₂ to dienes.

In conclusion, let us note certain special methods that make it possible to obtain NO addition products of alkenes.

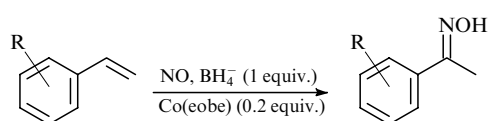
For example, the addition of the NO-containing cobalt(II) complex **31** to mono- and disubstituted alkenes has been reported.⁴¹ The resulting adducts **32** can be reduced to the corresponding diamines.



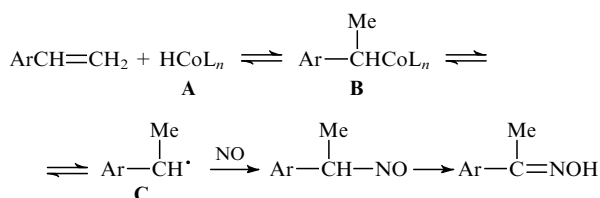


$R^1, R^2 = \text{H, Alk, Ar}; R^1 - R^2 = (\text{CH}_2)_n; n = 3, 4.$

The ability of NO to add to alkenes by catalysis with Co(II) complexes is well known. The method involves the initial addition of the hydride complex **A** generated *in situ* to an alkene, dissociation of the resulting metal–carbene adduct **B** to release the alkyl radical **C** and recombination of the latter with NO. The resulting nitroso compound quickly rearranges into an oxime.⁴² In this case, the involvement of coordination-bound NO in the process can be ruled out,⁴³ since the addition of a stronger ligand, *viz.*, pyridine, does not inhibit the reaction.

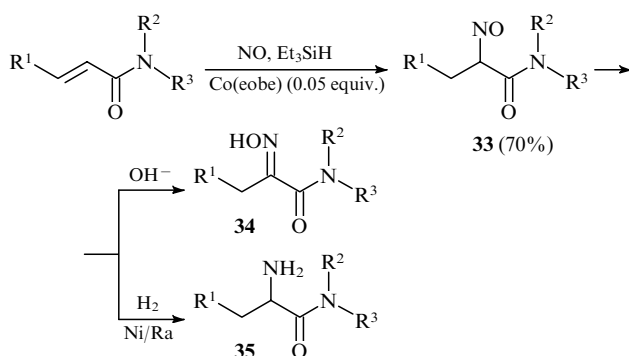


$R = \text{Alk, OAlk, Hal}; \text{Co(eobe)} = \text{EtO}_2\text{C}-\text{C}_5\text{H}_3\text{N}_2\text{O}_2-\text{CO}_2\text{Et}.$



The efficiency of this approach was first demonstrated with the transformation of substituted styrenes into the corresponding oximes as an example.^{42, 43} In polar aprotic solvents, the reaction occurs slowly and in moderate yields (40%–60%). The best results were obtained in a mixture of dimethoxyethane and Pr^iOH . In this case, acetophenone oxime was obtained in 83% yield.

The method also proved to be efficient for the nitrosation of α, β -unsaturated amides. In this case, the Co(II) hydride complex was generated using Et_3SiH . The resulting nitroso compounds **33** can be transformed into oximes **34** or reduced with Raney nickel into amino acid derivatives **35**.⁴⁴

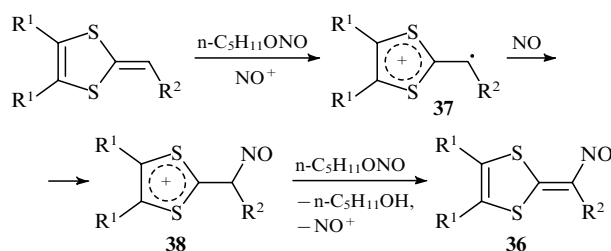


$R^1 = \text{H, Alk}; R^2, R^3 = \text{Alk, Ar, ArCH}_2.$

III. Reactions of alkenes with alkyl nitrites

Alkyl nitrites react only with double bonds incorporated in readily polarisable conjugated systems. In particular, it was found that dithiafulvenes react with *n*-pentyl nitrite in CH_2Cl_2 to give the

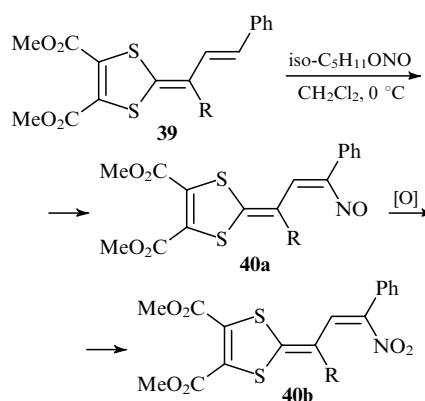
corresponding nitroso compounds **36** in 60%–70% yields.^{45–47} Diselenafulvenes react with alkyl nitrites in a similar way.⁴⁸



$R^1 = \text{CO}_2\text{Me, Ar, Me, SMe}; R^2 = \text{Ar, COMe, CHO}.$

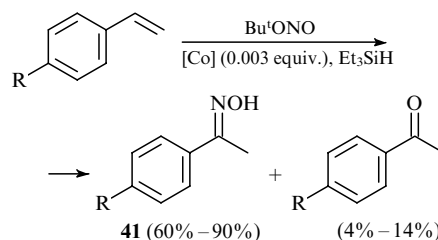
The proposed reaction mechanism⁴⁵ involves the generation of the NO^+ cation from nitrite; however, owing to the low electrophilicity of the cation, it can only participate in electron transfer; in such a case, it is oxidised into NO. The alkene is converted into the radical cation **37**. Recombination of the latter with NO followed by the reaction of the resulting cation **38** with a second nitrite molecule gives the nitro compound **36** and pentanol; the nitronium ion is regenerated.

Dithiafulvene derivatives **39** are even more reactive with respect to nitrites; under mild conditions, they give unstable nitroso compounds **40a**, which are readily oxidised with atmospheric oxygen into the corresponding nitro derivatives **40b**.⁴⁹



$R = \text{Me, CF}_3, \text{CN}.$

Nitrosation of less reactive substrates with alkyl nitrites can only be carried out under catalysis with Co(II) complexes; this method turned out to be more efficient and more convenient in preparative synthesis than the Co(II)-catalysed reaction of alkenes with NO (see Section II). This is obviously due to the higher electrophilicity of the NO^+ cation in comparison with NO and also due to the fact that this reaction is carried out under homogeneous conditions. For example, nitrosation of substituted styrenes in the presence of catalytic amounts of a porphyrin–Co(II) complex and Et_3SiH as a reducing agent gives oximes **41** with an admixture of the corresponding acetophenones.⁵⁰

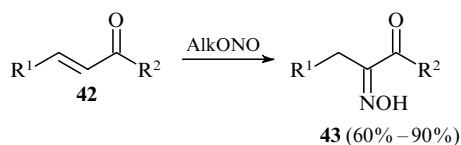


$R = \text{H, Me, Cl, CO}_2\text{Me, NO}_2.$

The use of Fe(III) acetylacetonate as a catalyst has also been reported.⁵¹ In this case, mono- and dialkyl-substituted alkenes

gave dimers of the corresponding nitroso compounds in ~ 50% yields.

The use of Co(II)-based catalysts for the nitrosation of linear alkenes **42** with electron-withdrawing substituents by alkyl nitrites was found to be very efficient. The reaction gives oximes **43** in high yields.⁵⁰ Dienes **44** as substrates give the corresponding conjugated oximes.⁵⁰ It was noted that the yields of oximes **43** can be increased noticeably using PhSiH₃ as the reducing agent.^{52, 53}

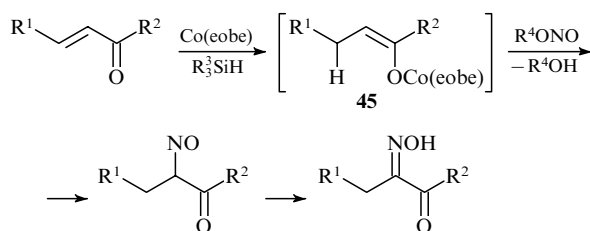


R¹ = H, Alk; R² = H, Alk, OAlk.



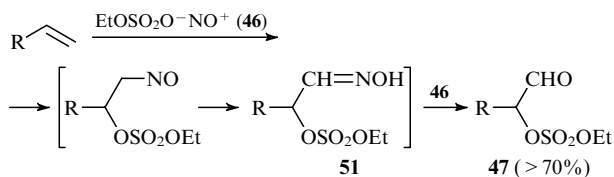
R¹ = H, Bu^t, NR₂⁺, OAlk, OAr; R² = Alk.

Styrenes probably react with nitrites according to a mechanism similar to that suggested for the reaction with NO, whereas the conversions of α,β-unsaturated carbonyl compounds presumably involve cobalt enolate **45**.⁵³

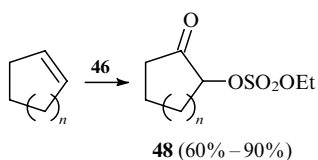


R¹ = H, Alk; R² = Alk, Ph, NMePh, OAlk, OBn; R³ = Et, Ph; R⁴ = Alk.

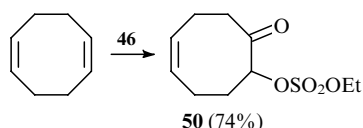
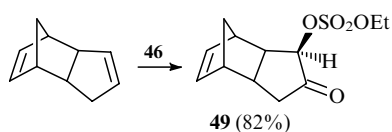
There is yet another method for using alkyl nitrites for the nitrosation of alkenes.^{54, 55} Thus, a highly reactive intermediate is generated from EtONO upon treatment with SO₃; it is believed to have an ionic structure, *viz.*, EtOSO₂O⁻-NO⁺ (**46**). The reaction of an excess of the reagent **46** with various alkenes affords sulfates of α-hydroxy aldehydes (**47**) or ketones (**48–50**).



R = H, Alk.

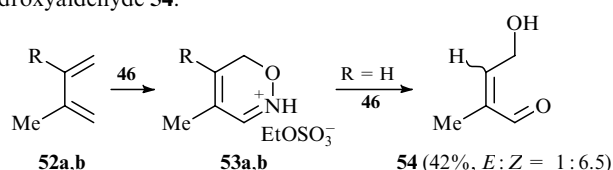


n = 1, 2, 4.



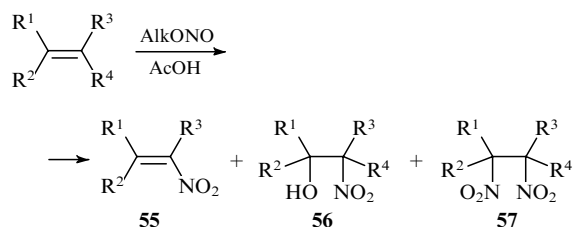
The reagent **46** also serves as an oxidant which converts the intermediate oximes **51** into the corresponding carbonyl compounds. The proposed reaction mechanism is confirmed by the fact that it is possible to isolate dimers of nitroso intermediates using one equivalent of the reagent **46** with respect to the alkene. This reaction was found to be chemoselective. In particular, only the least hindered double bond is involved in the cyclopentadiene dimer; in the case of cyclooctadiene, the monoadduct **50** can be obtained in high yield.

The reaction of isoprene (**52a**) or dimethylbutadiene (**52b**) with a stoichiometric amount of the reagent **46** ends in the formation of the corresponding oxazonium salts **53a,b**. The reaction of the salt **53a** with an excess of the reagent affords hydroxyaldehyde **54**.



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

In conclusion, we would like to note the ability of alkyl nitrites to generate reactive species in acidic media, which react with alkenes. For example, treatment of acyclic di-, tri- and tetrasubstituted alkenes with pentyl or butyl nitrite in AcOH gives mixtures of products **55–57**, the composition of which varies depending on the substrate structure.⁵⁶

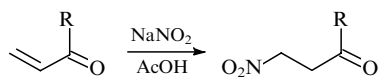


R ¹	R ²	R ³	R ⁴	Yield (%)		
				55	56	57
Ph	Ph	H	H	27	25	–
Ph	Me	H	H	–	33	–
Me	CO ₂ Me	H	H	–	20	–
Et	Et	Me	H	–	23	43
Me	Me	Me	Me	–	6	30

IV. Reactions involving nitrous acid salts

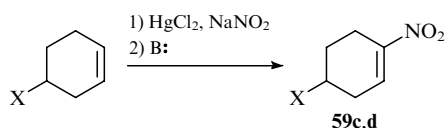
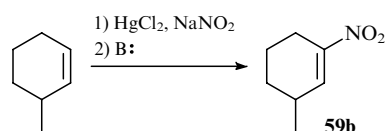
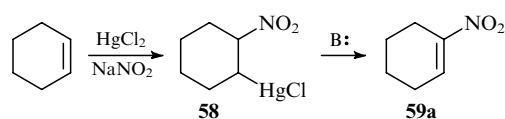
Nitrous acid salts can serve as sources of various neutral species (NO, NO₂, N₂O₃, N₂O₄) and ions (NO₂⁻, NO₂⁺) resulting from disproportionation of unstable nitrous acid formed.⁵⁷ Each of these species can, in one way or another, react with alkenes.

For example, the NO₂⁻ anion can undergo Michael-type addition to vinyl ketones on treatment of the latter with NaNO₂ in AcOH, giving β-nitro derivatives in satisfactory yields.⁵⁸

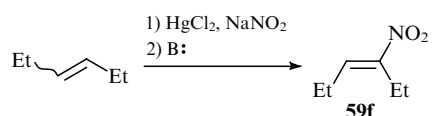
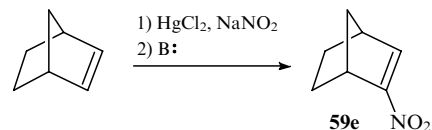


R = Me (82%), Et (46%), Prⁱ (42%), Prⁿ (57%), Buⁿ (65%), n-C₅H₁₁ (68%).

Furthermore, procedures based on the reaction of NO₂⁻ and a carbocation generated from an alkene are also known. For example, chloromercuration of mono- and disubstituted alkenes in the presence of NaNO₂ gives adducts of the type **58**, which can be transformed without isolation into the corresponding nitroalkenes **59a–f** in ~80% yields upon treatment with a base.⁵⁹ Mercury perchlorate can be used instead of HgCl₂.⁶⁰ It should be noted that reactions with hex-3-enes stereoselectively give the *E*-nitro derivative **59f** irrespective of the configuration of the starting alkene.



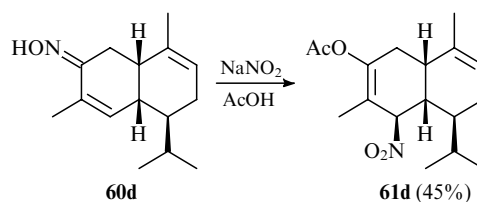
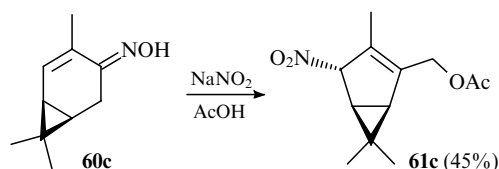
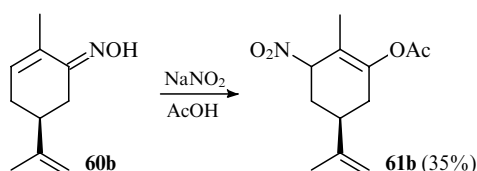
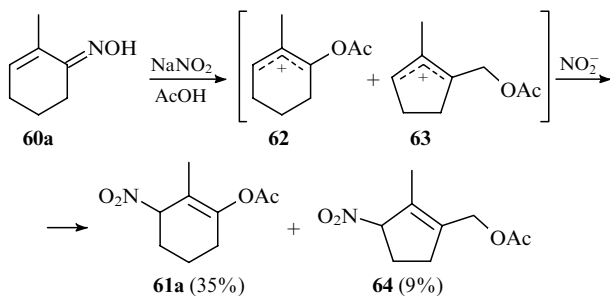
X = CN (**c**), CO₂Me (**d**).



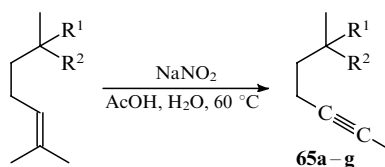
B: is a base

The conversion of conjugated oximes **60a–d** into nitro acetates **61a–d** on treatment with NaNO₂ in acetic acid was explained by reactions of allylic cations of the types **62** and **63** with NO₂⁻ (see Ref. 61). In this case, the system NaNO₂–AcOH (HNO₂) plays a double role, *viz.*, it also cleaves oximes to give carbenium intermediates.

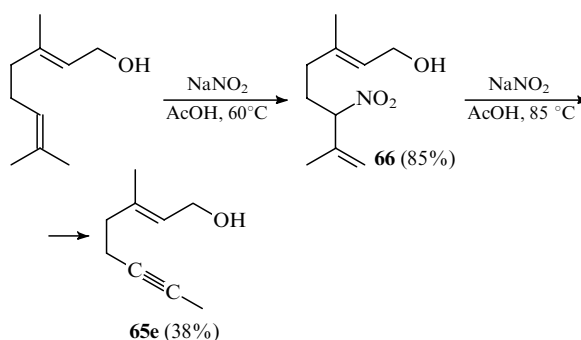
Oxime **60a** gave, in addition to the main product **61a**, the minor cyclopentene **64** corresponding to the carbocation **63**. The predominant pathway of the reaction with the carene derivative **60c** results in the nitro derivative **61c**.



In 1985, Abidi⁶² reported an unusual transformation of the isopropylidene fragment of linear monoisoprenoid derivatives into a methylethynyl fragment, which occurred upon treatment with NaNO₂ in aqueous acetic acid (see also the subsequent papers by Abidi^{63,64}). It should be noted here that later studies of this reaction (formal methane elimination) with the same and related substrates^{65,66} could not reproduce the previously reported^{62–64} high yields (60%–90%) of the corresponding methylacetylenes **65a–g**. For example, the yield of the acetylene **65e** from geraniol was no higher than 35%.⁶⁵



R¹ = H, R² = (CH₂)₂OH (**a**), CH₂CHO (**b**); R¹ = CH=CH₂, R² = OH, OAc, OMe (**c**); R¹, R² = (*E*)-CHCHO (**d**), (*E*)-CHCH₂OH (**e**), (*E*)-CHCH₂CH₂C(O)Me (**f**), (*E,E*)-CHCH₂CH₂C(Me)=CH₂CH₂OH (**g**) *etc.*

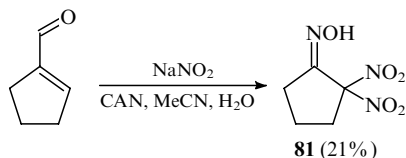


It was found that this reaction initially yields the nitro derivative **66**. Its treatment with sodium nitrite in acetic acid affords acetylene **65e** with evolution of an equivalent amount of CO₂.

Attempts to rationalise the mechanism of this process^{65,66} led to the assumption that oximes of the type **67** are precursors of acetylenes **65**. It is well known that nitrosation of oximes of conjugated aliphatic ketones can give pyrazole derivatives that can subsequently undergo conversions indicated in the scheme.⁶⁷ In fact, oximes **67** (obtained by an independent synthesis) gave the corresponding alkynes **68** in up to 20% yields upon treatment with NaNO₂ in acetic acid.⁶⁶

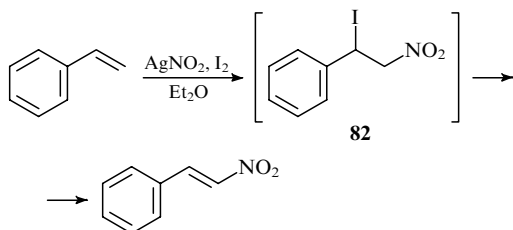
formed due to the stabilisation of the carbocation **80** upon the addition of MeCN.⁸⁰

Quite an unexpected result was obtained under similar conditions with cyclopentenecarbaldehyde as the substrate: the reaction yielded dinitrooxime **81**. It was shown using labelled $\text{Na}^{15}\text{NO}_2$ that the latter is the only source of nitrogen atoms incorporated into compound **81**.⁸¹

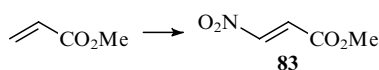


There is yet another approach to the use of nitrous acid salts as sources of reactive intermediates: nitrile halides, *e.g.*, nitrile iodide, are generated *in situ* from the salts under the action of halogens. Nitrile iodide was first generated using the reaction of AgNO_2 with I_2 .^{82,83} Theoretically, it may be assumed that the heterolysis of nitrile iodide occurs with formation of either NO_2^+ ions and I^- , or NO^+ and I^- ; furthermore, homolysis into free radicals is also possible (see Ref. 82 and references cited therein).

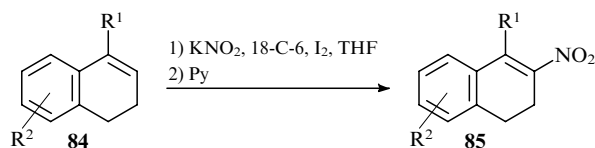
The reaction of AgNO_2 with I_2 in the presence of an alkene, *e.g.*, styrene, results in the labile nitro iodide **82**, which readily undergoes dehydroiodination on treatment with a base to give ω -nitrostyrene.⁸² This regioselectivity of the process suggests that the reagent formed cannot react with the alkene as iodonium nitrite INO_2 .



With methyl acrylate as the substrate, a terminal nitro derivative **83** was obtained after treatment of the reaction mixture with a base; it may be concluded on this basis that INO_2 in this process is not an equivalent of NO_2^+ but rather a source of NO_2 radicals.



The use of more accessible sodium and potassium nitrites instead of AgNO_2 was a further development of this method.^{84–86} For example, treatment of a series of mono- and disubstituted alkenes with NaNO_2 and I_2 in an $\text{EtOAc}-(\text{CH}_2\text{OH})_2-\text{H}_2\text{O}$ mixture afforded the corresponding α,β -unsaturated nitro compounds in high yields.⁸⁴ The use of phase-transfer catalysis in order to intensify the process was also described. In particular, dihydronaphthalene derivatives **84** reacted with potassium nitrite and iodine in the presence of a crown ether (18-C-6) to give (after treatment with pyridine) nitro derivatives **85** in 50%–90% yields.⁸⁵ It was noted that the reaction occurred much faster under sonication.



$\text{R}^1 = \text{H, Ph}; \text{R}^2 = \text{H, OMe}$.

It is also of note that nitro derivatives can be obtained using the $\text{NaNO}_2-\text{I}_2-\text{CuO}-\text{HBF}_4$ system. The efficiency of this approach was demonstrated by the conversion of substituted

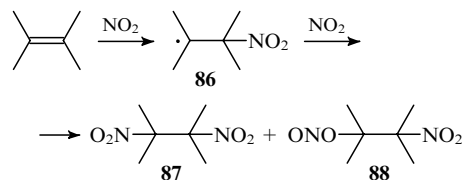
styrenes into nitrostyrenes; additional treatment with a base was not required under these conditions.⁸⁶

V. Reactions of NO_2 with alkenes

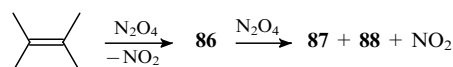
The reactions of NO_2 with alkenes have mostly been considered in the reviews published previously;^{8–12} therefore, this chapter only discusses the latest publications not included in those reviews.

To date, a number of mechanisms have been suggested for reactions of NO_2 with alkenes. Which one predominates depends on the reaction conditions. In fact, according to kinetic data, if the process is carried out in non-polar solvents, the reaction becomes second-order with respect to NO_2 with an increase in its concentration.⁸⁷ At low NO_2 concentrations, the formation of the alkyl radical **86** (pathway *a*) is the rate-determining step. Subsequently, the radical **86** recombines with the second NO_2 molecule to give dinitro compound **87** and nitro nitrite **88**. In more concentrated solutions, dimerisation of NO_2 increases the concentration of N_2O_4 , which obviously can also add to the alkene to give the radical **86** (pathway *b*), thus increasing the reaction order. Furthermore, one may not rule out the possibility that the alkyl radical **86** reacts with N_2O_4 to give the same products, *viz.*, **87** and **88**.⁸⁸

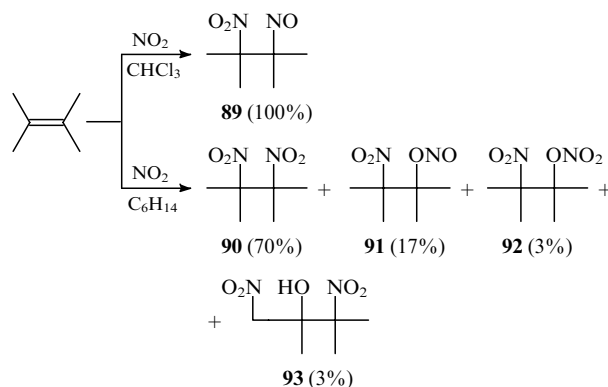
Pathway *a*



Pathway *b*

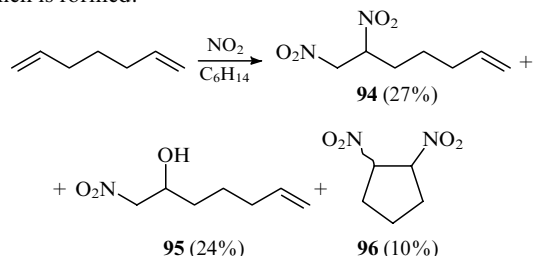


If the reaction is carried out in a more polar medium, another process starts to play a considerable role; it occurs by a heterolytic mechanism due to the presence of nitrosyl nitrate (NO^+NO_3^-) in solutions of NO_2 or N_2O_4 .^{89,90} The possibility of the existence of this compound was substantiated by calculations.^{91,92} The fact that alkenes can react with nitrosyl nitrate by a heterolytic mechanism follows from the formation of the corresponding nitro nitroso compounds.^{93,94} For example, treatment of 2,4-dimethylhexene with a solution of NO_2 in CHCl_3 results only in the nitro nitroso adduct **89**, whereas in hexane, this alkene gives a mixture of compounds **90–93**, which are formed in the reaction occurring by a homolytic mechanism.⁹⁴ The formation of the dinitro alcohol **93** results from the ability of nitrogen dioxide to abstract hydrogen from the carbon atom adjacent to the double bond to give an allylic radical. This process starts to play a significant role at very low NO_2 concentrations.⁹⁵ For example, a study of reactions of NO_2 with unsaturated fatty acids mainly

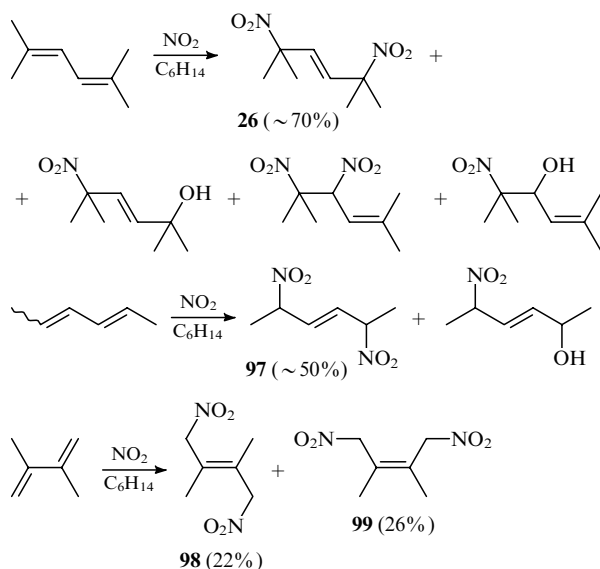


revealed allylic nitration products and the corresponding allyl hydroperoxides.^{96, 97}

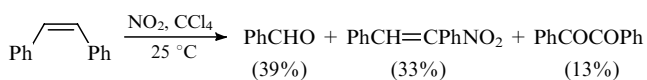
It should be noted that treatment of hexa-1,5-diene with a dilute solution of NO_2 in hexane gives not only the dinitro compound **94** and the nitro alcohol **95** but also the isomeric 1,2-dinitrocyclopentanes **96**.⁹⁸ The formation of the latter suggests that two NO_2 molecules can add to the diene independently; this is accompanied by intramolecular recombination of the biradical which is formed.



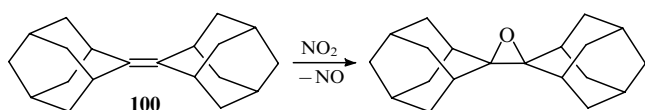
Conjugated dienes mostly give dinitro derivatives **26**, **97–99** under these conditions.⁹⁸ A small amount of compound **26** is also formed in the reaction of 2,5-dimethylhexa-2,4-diene with NO_2 .³³



NO_2 manifests considerable oxidising properties with respect to some substrates. For example, (*Z*)-stilbene reacts with NO_2 in CCl_4 to give benzaldehyde as the main reaction product formed due to oxidative fragmentation.⁹⁹



One should also note the interesting version of epoxidation of the sterically hindered tetrasubstituted alkene **100** on treatment with NO_2 .¹⁰⁰ The latter is reduced to NO . Using the smooth oxidation of NO to NO_2 , this reaction can be carried out either with a stoichiometric or a catalytic amount of NO_2 in the presence of oxygen.

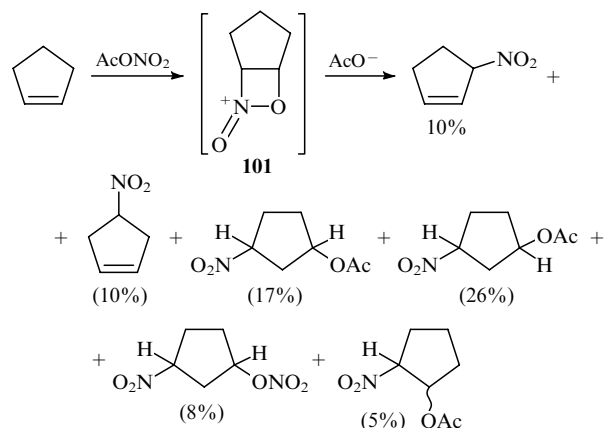


VI. Reactions of the NO_2^+ cation and its equivalents with alkenes

The NO_2^+ cation is generated from acetyl nitrate, which is usually obtained *in situ* from Ac_2O and concentrated nitric acid. It should be noted that the previously suggested mechanism of electrophilic

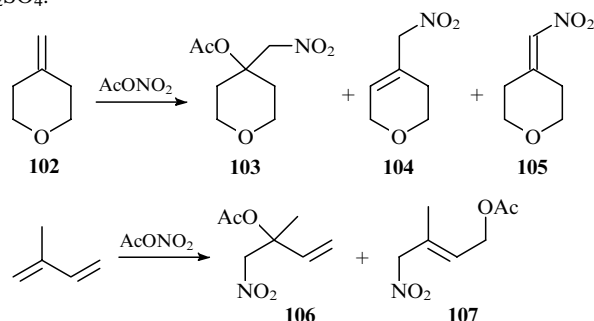
addition of NO_2^+ to a double bond to give a classical carbocation does not often allow one to explain the diversity of the resulting products and their structures (see, *e.g.*, Ref. 92 and references cited therein).

For example, the reaction of cyclopentene with AcONO_2 results in a mixture of at least six compounds. This mixture does not contain conjugated 1-nitrocyclopent-1-ene, the most thermodynamically favourable compound, the formation of which, due to deprotonation of the corresponding α -nitrocarbocation, could be expected.⁹² Analysis of these results made it possible to assume that this process can occur through initial [2+2]-cycloaddition of NO_2^+ to the double bond to give the cyclic cationoid intermediate **101**. Its subsequent reaction with the acetate anion, rearrangement and deprotonation of the intermediates result in a wide range of products. This hypothesis was also confirmed by semiempirical calculations for the ethylene- NO_2^+ system, according to which the cyclic ion of the type **101** corresponds to one of the potential energy minima.^{92, 101–103}



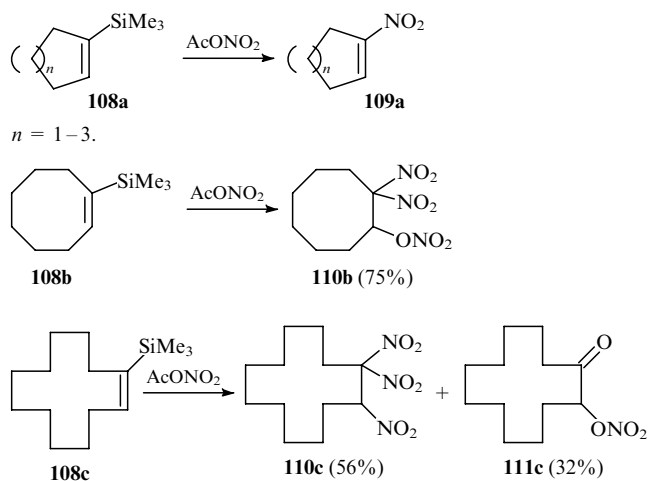
In fact, reactions of various alkenes with NO_2^+ generally yield allylic rather than conjugated nitro compounds. In particular, allylic nitro derivatives were isolated from a mixture of products obtained upon treatment of a derivative of an antibiotic milbemycin with acetyl nitrate.¹⁰⁴

Nitration of 4-methylidenetetrahydropyran **102** with nitric acid in Ac_2O gave the nitro acetate **103** as the major product; the ratio of the allylic (**104**) and vinylic (**105**) regioisomers in the reaction mixture was 2:1.¹⁰⁵ The reaction of acetyl nitrate with isoprene afforded a mixture of 1,2- (**106**) and 1,4-addition (**107**) products; the tertiary acetate **106** smoothly isomerises into the primary acetate **107** on treatment with a catalytic amount of H_2SO_4 .^{106, 107}

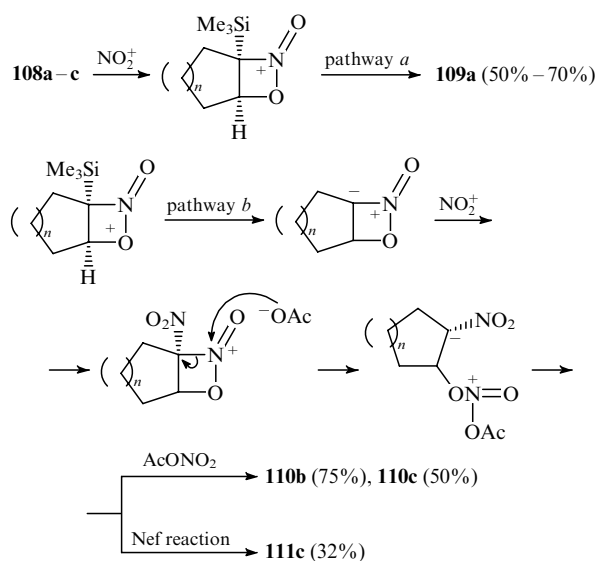


One of the most convincing confirmations of the four-centred addition mechanism of NO_2^+ to alkenes was obtained in a study of the reaction of acetyl nitrate with 1-trimethylsilylcycloalkenes **108a–c**, which resulted in different products depending on the ring size.¹⁰⁸ For instance, cyclopentene, cyclohexene and cycloheptene derivatives **108a** only give unsaturated nitro compounds **109a** in good yields (50%–70%). Under similar conditions, 1-trimethylsilylcyclooctene (**108b**) gives the dinitro nitrate **110b**;

the cyclododecadecene derivative **108c** gave the dinitro nitrate **110c** and the ketone **111c**.

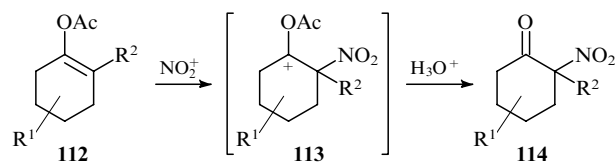


In these reactions, the trimethylsilyl substituent serves as the directing group in the addition of NO_2^+ to the double bond. The trimethylsilyl group is a better leaving group than hydrogen; this ensures the eventual formation of the conjugated nitro alkene **109a** (pathway *a*). It is believed¹⁰⁸ that the spatial arrangement of the trimethylsilyl substituent in large rings is unfavourable for the E_2 elimination. As a result, it is eliminated by the E_1 mechanism; the resulting carbanion is then converted to the products **110b,c** and **111c** (pathway *b*) on treatment with acetyl nitrate.



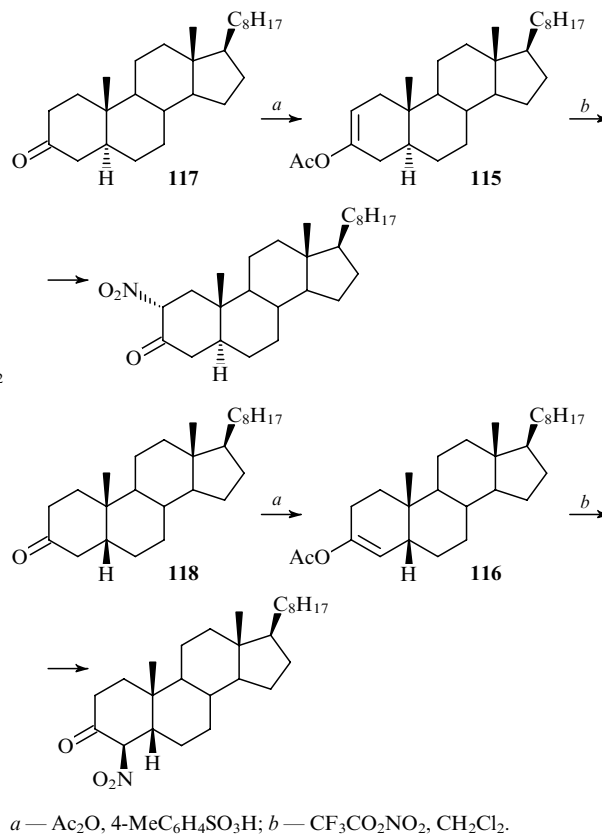
More examples are known in which acetyl nitrate reacts selectively with unsaturated substrates containing functional substituents at the double bond.

For example, the reaction of AcONO_2 with alkyl-substituted 1-acetoxycyclohexenes **112**, which occurs through deacetylation of the cation **113**, affords α -nitrocyclohexanones **114** in 70%–90% yields.¹⁰⁹ The yields of the corresponding ketones were subsequently increased to 80%–100% using trifluoroacetyl nitrate.¹¹⁰

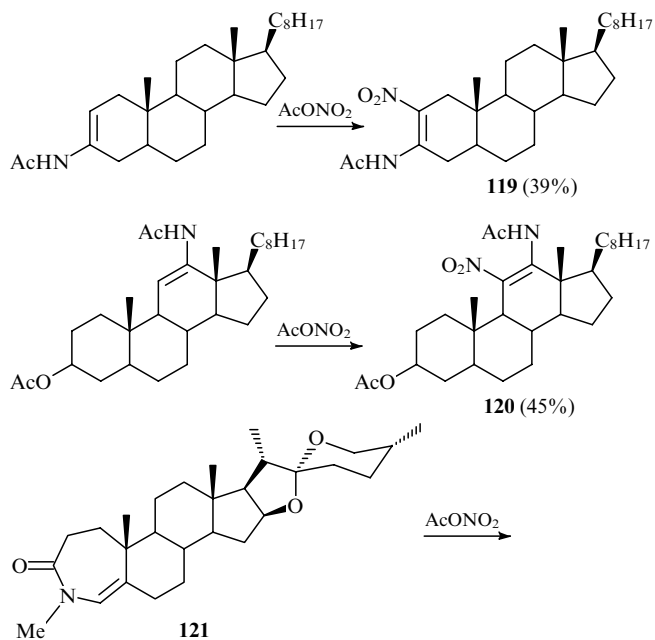


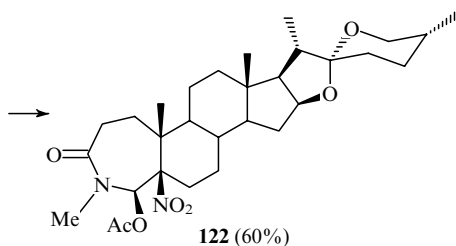
$\text{R}^1 = \text{Alk}, \text{R}^2 = \text{H}, \text{Me}.$

A similar reaction of enol acetates **115** and **116** was used for the regio- and stereoselective incorporation of a nitro group into isomeric ketosteroids **117** and **118**,¹¹¹ the direction of their enolisation is governed by the type of fusion of rings A and B.

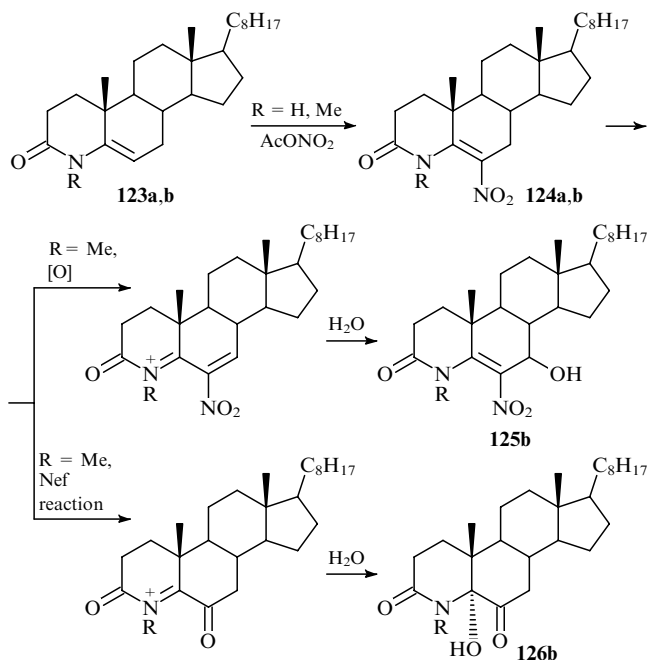


In enamides of the steroid series, the AcHN group directs the attack of the nitronium cation to the β -position with respect to the double bond, giving the nitro enamides **119** and **120**.¹¹² The enamide **121** gives the nitro acetate **122** under the same conditions.¹¹³



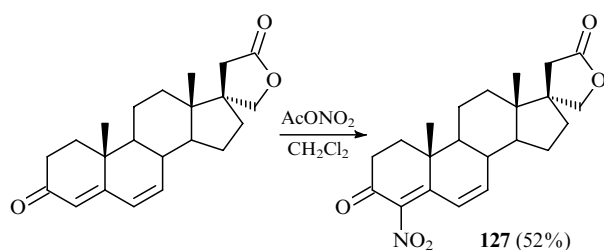


The nitration of the enamides **123a,b** gives different products, depending on the substituent R at the nitrogen atom.¹¹⁴ The unsubstituted amide **123a** yields the nitro alkene **124a** as the main product (55%), whereas the methylated derivative **123b** gives a mixture of the nitro alcohol **125b** and hydroxy ketone **126b** in moderate yield (20%). The difference between the reactivities of the amides **123a,b** is explained by the fact that the nitro compound **124a** can be stabilised due to the formation of an intramolecular hydrogen bond. The methyl derivative **124b** is unstable and undergoes further conversions as a result of the Nef reaction and allylic oxidation. In the case of the amide **124a**, both of the processes also occur, but the yield of the minor products is no higher than 15%.



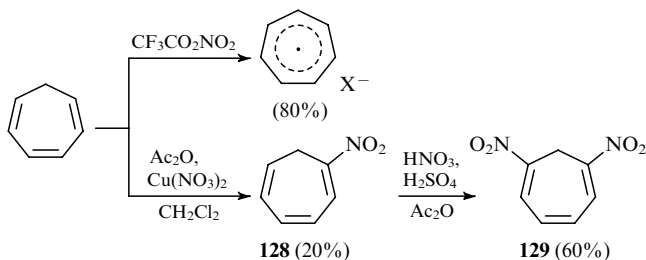
R = H (a), Me (b).

Probably, a unique example of a reaction of acetyl nitrate with a diene system conjugated with a carbonyl group has been reported by German chemists.¹¹⁵ The nitration of a pregnane ketosteroid, *viz.*, a canrenone derivative, unexpectedly resulted in a 4-nitro compound **127**, whereas the 6,7-double bond in the original dienone remained intact.



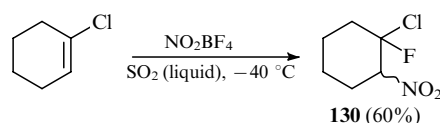
Furthermore, the unusual behaviour of cycloheptatriene is also noteworthy. Its conjugated system is oxidised on treatment with CF_3CONO_2 to give a tropylium cation.¹¹⁶ On the other hand, the reaction of cycloheptatriene with copper nitrate in Ac_2O gives

the 1-nitro derivative **128** in low yield.¹¹⁷ The role of copper ions is probably to inhibit the oxidation process. Subsequent nitration of the mononitro derivative **128** with acetyl nitrate gave the dinitro compound **129**.

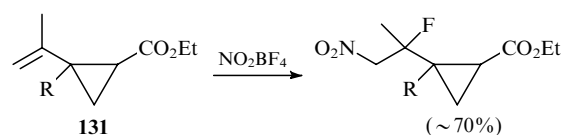


Nitronium tetrafluoroborate is yet another source of NO_2^+ known for a long time. As noted in an earlier review,¹¹⁸ its reaction with alkyl-substituted alkenes is not straightforward due to the formation of very reactive cationoid intermediates and can be accompanied by polymerisation. We will consider certain examples of reactions of alkenes with NO_2BF_4 which have not been covered in the review by Guk *et al.*¹¹⁸ or in later reviews.

Obviously, the nature of the products formed in the reactions of alkenes with NO_2BF_4 depends on the structure and environment of the cationoid centre, which appears in a reacting molecule in the first step of the process. For example, the reaction of 1-chlorocyclohexene with NO_2BF_4 yields exclusively products of the formal NO_2F addition, *viz.*, compound **130** (with the ratio of the *cis* and *trans* isomers equal to 4:1).¹¹⁹

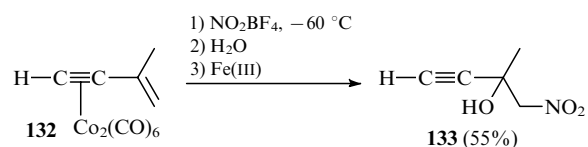


Isopropenyl derivatives of cyclopropanecarboxylic acid **131** react with NO_2BF_4 in a similar way.¹²⁰ Surprisingly, this does not cause a skeletal rearrangement typical of carbocations with the cyclopropyl substituent.



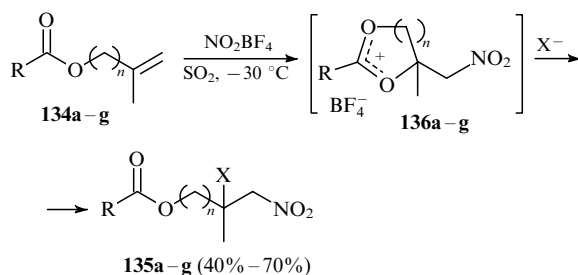
R = H, Me.

A different pattern is observed in the reaction of nitronium tetrafluoroborate with the isopropenylacetylene–octacarbonyl-dicobalt complex **132**. The alkynedicobaltoctacarbonyl residue in this compound stabilises the carbenium ion formed due to the NO_2^+ attack on the double bond.¹²¹ Subsequent hydrolysis of the reaction mixture and oxidation of the cobalt carbonyl complex gives the nitro alcohol **133**.



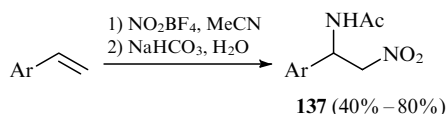
Furthermore, reactions of allylic esters (**134a–d**)¹²² and homoallylic esters (**134e–g**)¹²³ with nitronium tetrafluoroborates followed by hydrolysis have been reported; they gave mixtures of 2-fluoro nitro alkane (X = F) and β -nitro alcohol (X = OH) derivatives **135a–g**. In this case, the overall yield and composition of the products depend on the bulk of the acyl substituent R. The reaction presumably occurs *via* cyclic cationoid intermediates **136a–g**, which are split by fluoride or hydroxide ions to give the

final products. The formation of these intermediates was detected using low-temperature NMR spectroscopy.¹²³

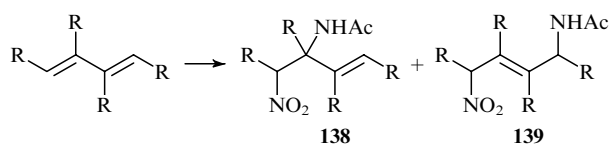


Compound 134	R	n	Product ratio 135a–g (X = F/X = OH)
a	Me	1	95/5
b	Et	1	70/30
c	Pr ⁿ	1	65/35
d	Pr ⁱ	1	75/25
e	Me	2	95/5
f	Pr ⁿ	2	75/25
g	Pr ⁱ	2	55/45

Acetonitrile may serve as the nucleophile which completes the reaction of alkenes with NO_2BF_4 . For example, low-temperature treatment of substituted styrenes with nitronium tetrafluoroborate in MeCN followed by decomposition with saturated aqueous NaHCO_3 afforded the corresponding nitro acetamides **137** obviously formed by the Ritter reaction.¹²⁴

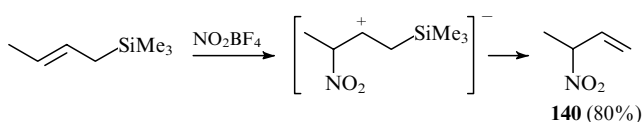


Conjugated dienes undergo similar conversions to give 1,2- (**138**) and 1,4-addition (**139**) products in approximately 1 : 1 ratios (the overall yield is 70%–90%). In this case, nitronium tetrafluoroborate was generated by *in situ* anodic oxidation of N_2O_4 in the presence of LiBF_4 .¹²⁵

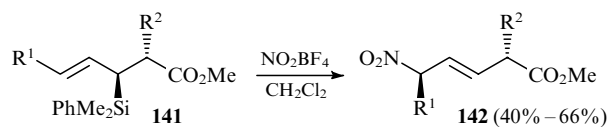


R = H, Me.

Finally, the reaction of NO_2BF_4 with allylsilanes deserves attention. In particular, it was found that treatment of *trans*-but-2-enyltrimethylsilane with nitronium tetrafluoroborate results in the allylic nitro compound **140**, which is formally a reaction product by the S_E' mechanism.¹²⁶ It is believed that compound **140** is formed by electrophilic addition of the NO_2^+ cation to the double bond followed by elimination of the trimethylsilyl group from the carbenium intermediate.

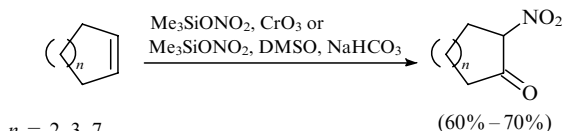


Subsequently,¹²⁷ potential synthetic applications of this approach were demonstrated. It was found that treatment of chiral (*E*)-crotylsilanes **141** with NO_2BF_4 converts them to allylic nitro derivatives **142**. The reaction occurs with high diastereoselectivity (*de* > 90%), since the stereochemistry of the forming chiral centre is controlled by the configuration of the asymmetric centre with the silyl substituent.

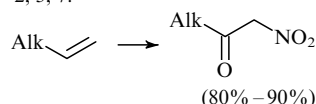


$\text{R}^1 = \text{Alk}$; $\text{R}^2 = \text{H, Me, All, OMe}$.

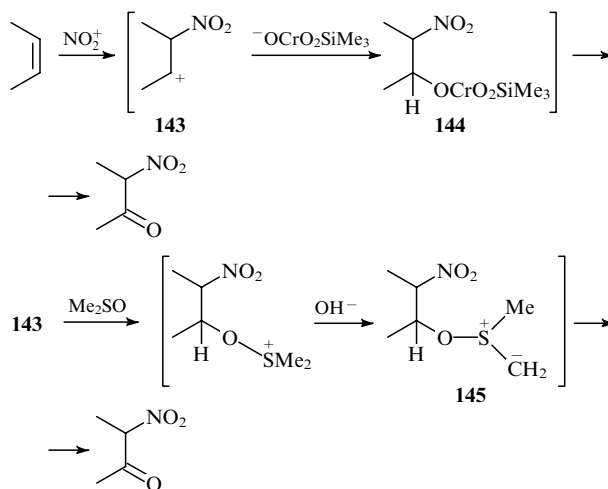
The NO_2^+ cation can also be generated from $\text{Me}_3\text{SiONO}_2$, which reacts with linear or cyclic alkenes in the presence of CrO_3 or DMSO to give α -nitro ketones in high yields.^{128, 129}



$n = 2, 3, 7$.

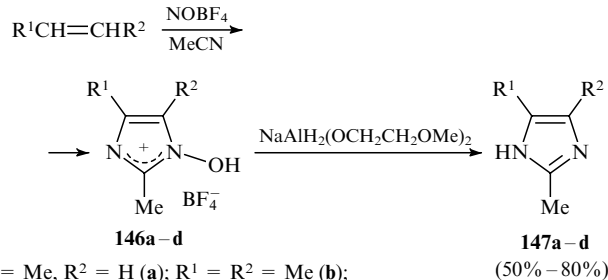


It is believed that the reaction of $\text{Me}_3\text{SiONO}_2$ with CrO_3 generates $\text{NO}_2\text{OCrO}_2\text{SiMe}_3$ *in situ*; the latter is a source of NO_2^+ and of an oxidant, *viz.*, the $^-\text{OCrO}_2\text{SiMe}_3$ anion. The latter reacts with the carbenium ion **143**, which is originally formed upon the attack of the NO_2^+ cation on the double bond to give intermediate **144**. A similar intermediate was postulated in the oxidation of alcohols with chromium-containing reagents. An analogous role is played by DMSO, which reacts with the carbocation **143** *via* an oxysulfonium salt to give the ylide **145**, a well-known intermediate in the Moffatt–Swern oxidations.



VII. Reactions of alkenes with NO^+

Reactions of NO^+ with alkenes are accompanied by further transformations of reactive β -nitroso carbocations formed initially, and the nature of the products depends on the structure of the substrate. For example, reactions of terminal and internal alkenes with nitrosonium tetrafluoroborate in acetonitrile give *N*-hydroxyimidazolium tetrafluoroborates **146a–d**.¹³⁰ Substi-

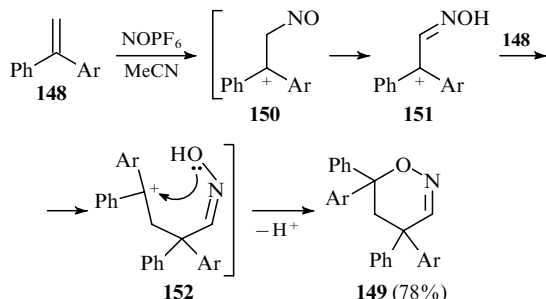


$\text{R}^1 = \text{Me}, \text{R}^2 = \text{H}$ (**a**); $\text{R}^1 = \text{R}^2 = \text{Me}$ (**b**);

$\text{R}^1 = \text{Ph}, \text{R}^2 = \text{H}$ (**c**); $\text{R}^1 - \text{R}^2 = (\text{CH}_2)_4$ (**d**).

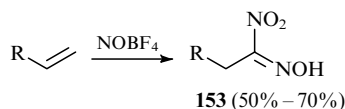
tuted imidazoles **147a–d** can be obtained in high yields by hydride reduction of the tetrafluoroborates **146**.

Arylalkenes react with nitrosonium tetrafluoroborate or hexafluorophosphate in a different way. In particular, 1-(4-methoxyphenyl)-1-phenylethylene (**148**) gave substituted 1,2-oxazine **149** in acetonitrile in high yield.¹³¹ It is assumed that the reaction occurs *via* carbocationic intermediates **150–152**.



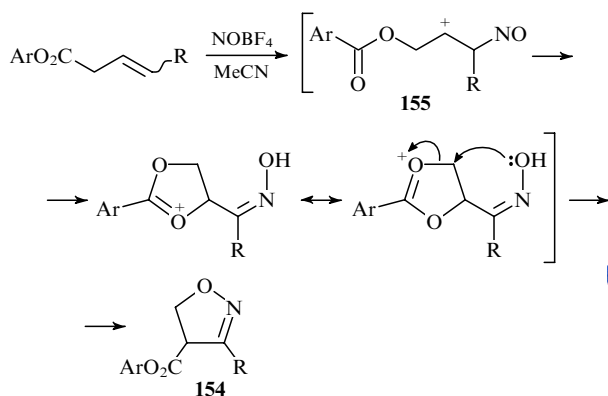
Ar = 4-MeOC₆H₄.

Vinylpyridines react with NOBF₄ in an unusual way to give nitrolic acids **153**,¹³² the mechanism of their formation under these conditions has not been elucidated so far.



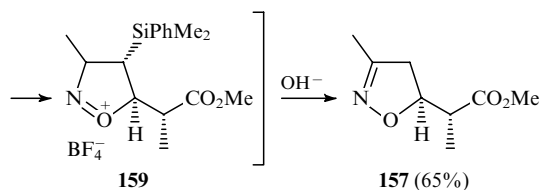
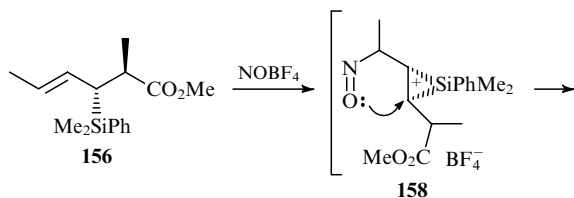
R = 2-, 3-, 4-pyridyl.

The reaction of allylic esters with NOBF₄ turned out to be a convenient method for the preparation of substituted 4,5-dihydroisoxazoles **154**.¹³³ The process occurs *via* the β-nitroso carbocation **155**, which is subsequently stabilised due to involvement of the arenecarboxylate residue.



R = H, Me, CH₂Br.

The transformation of the substituted crotylsilane **156** on treatment with NOBF₄ results in 4,5-dihydroisoxazole derivatives **157**.¹³⁴ Presumably, the reaction is stereocontrolled by the formation of a bridged cation **158** (σ,π-C–Si-conjugation), which is opened with total reversal of the configuration of the chiral centre at C(3) [C(5) in the product]. Heterocyclisation of the intermediate **158** gives the oxonium salt **159**, which is then deprotonated and protodesilylated by a base. The process occurs with high enantioselectivity and has high synthetic potential.



Thus, the results considered above demonstrate the wide prospects of nitrosation and nitration of alkenes for the synthesis of diverse functional derivatives, many of which are of interest as building blocks in organic synthesis.

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