

## Preparation of conjugated nitroalkenes: short review

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**Abstract:** Key protocols of the preparation of conjugated nitroalkenes were reviewed and critically discussed. It was established, that optimal strategy for the obtaining of target compounds are small molecules extrusion processes from saturated nitro-compounds. Among them, the most universal methodologies based on carboxylic acids elimination have been discussed, which provide for smooth applications.

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### Introduction

In the present time, conjugated nitroalkenes are very important building blocks in the organic synthesis [1-4]. This is possible due to their high global electrophilicity [5], and in the consequence, its high reactivity in the relation to nucleophilic agents. In particular, conjugated nitroalkenes are attractive partners for three atom components (TACs) [6] in [3+2] cycloaddition (32CA) reaction. These-type transformation open a possibility of the easy construction of wide range of nitro-functionalised five-membered heterocyclic systems based on nitrile N-oxides [7], imine N-oxides [8], imine N-tiooxides [9], azometineylides [10], tiocarbonylylides [11], diazocompounds [12], azides [13] and nitrylimines [14] (Fig.1.).



determine relatively low reaction selectivity. This is a consequence of many possible places within vinyl moieties, which can react with this type of nitration agents. Thus, the large number of products will be formed due to the direct nitration processes facing difficulties in isolation. In addition, not all nitration agents are usable for the substitution of vinyl hydrogen atoms. Actually, interaction between alkenes and nitrogen tetroxide leads to addition products instead of substitution products [25-27]. For example, relations between ethene and N<sub>2</sub>O<sub>4</sub> produce a mixture of 1,2-dinitroethane and 2-nitroethyl nitrite [26] (Fig.3.).

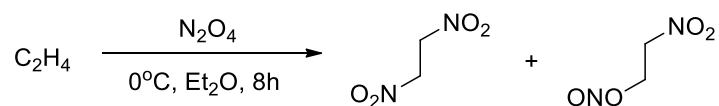


Fig. 3. Ethene nitration with nitrogen tetroxide.

Next, the nitration of 2-methyl-prop-1-ene using acetyl nitrate leads to mixture of different-type products, in which only small amount of unconjugated nitroalkene was detected [28] (Fig.4.).

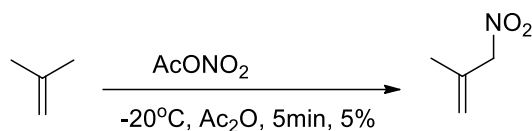


Fig. 4. The nitration reaction of 2-methyl-prop-1-ene using acetyl nitrate.

## Decomposition of saturated nitro-compounds

### Dehydration of 2-nitroalcohols

Nitro alcohols dehydration process without presence of any additional agents should be considered as rather difficult process from the preparative point of view. For example, the preparation of 2-nitro-but-1-ene and 2-nitro-pent-1-ene under these conditions require temperature in the range 290-350°C (!) [29,30]. So, in the practice, selected agents with the affinity for the water molecules was applied in the dehydration processes. For example, the dehydration of 1-chloro-1-nitro-2-ethanol in the presence of phosphorus pentoxide is realised at 150°C and give the expected nitroalkene with the satisfactory yield [31] (Fig.5.).

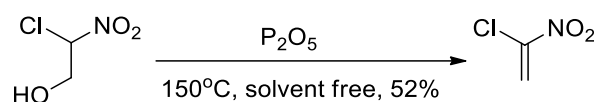


Fig. 5. Dehydration reaction of 1-chloro-1-nitro-2-ethanol in the presence of phosphorus pentoxide.

Similar transformation was described in the relation of the preparation of 1-bromo-1-nitroethene [32].

More effective hydrophilic agent in considered processes is a dicyclohexylcarbodiimide (DCHCDI) in the presence of the cuprum (I) chloride. For example, under these conditions, the dehydration of 2-nitropropan-1-ol is realised at 35°C and lead, with the satisfactory yield, to 2-nitroprop-1-ene [33]. Similar procedure can be applied inter alia for the preparation of 2-nitrohept-1-ene (Fig.6.).

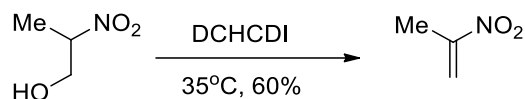


Fig. 6. Dehydration reaction of 2-nitropropan-1-ol with DCHCDI.

Some of 2-nitroalcohol dehydration processes are realised at lower temperature and without the participation of the hydrophilic agents. This scenario is most probable in the case of 2-nitroalcohols functionalised additionally by the second EWG group at 2-position. The example of these type transformation is the synthesis of 1,1-dinitroethene. The nitroalkene is formed due to high electrophilicity [34] as highly reactive and cannot exist as a stable compound. It can be trapped in situ using nucleophilic reagents such as cyclopentadiene [35] (Fig.7.).

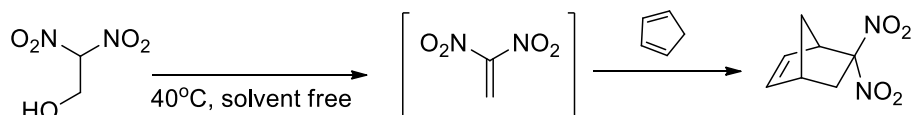


Fig. 7. 2,2-dinitroethanol dehydration process as a synthesis of 1,1-dinitroethene.

There is a similarity in the preparation and the stability of nitroalkenes with phenylsulfonyl, benzoyl as well as carboethoxy groups at the 1-position of nitrovinyl moiety [36,37].

2-nitroalcohols can generally be obtained using Henry condensation with the participation of aldehydes and primary nitroalkanes [38]. Some molecular systems could be converted under reaction conditions directly to respective nitroalkenes. The good example of these type transformations is the synthesis of 2-phenyl-1-cyano-1-nitroethene as well as its substituted analogues [39-42] (Fig.8.). It is an interesting, that this group of conjugated nitroalkenes are generally stable at room temperature.

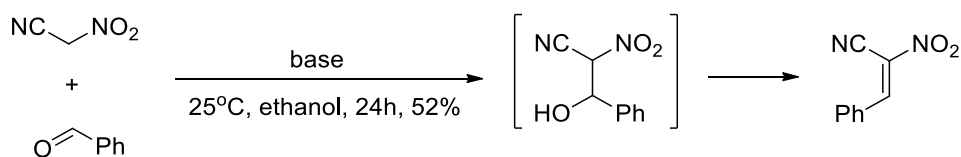


Fig. 8. Henry condensation as an example of a synthesis of 2-phenyl-1-cyano-1-nitroethene.

Nitroalkyl carboxylates decomposition

2-Nitroalcohols can be directly dehydrated, but from the preparative point of view, it is more convenient first to convert it for respective carboxylates which can be further converted in to nitroalkenes via carboxylic acid extrusion. For example, thermolysis of 2-benzoyloxy-1-phenyl-1-nitroethane give with the good yield 1-phenyl-1-nitroethene, which is not available to obtain in the other way [43] (Fig.9.). The starting ester can be easily obtained via simple reaction of respective nitro-alcohol with the benzoyl chloride.

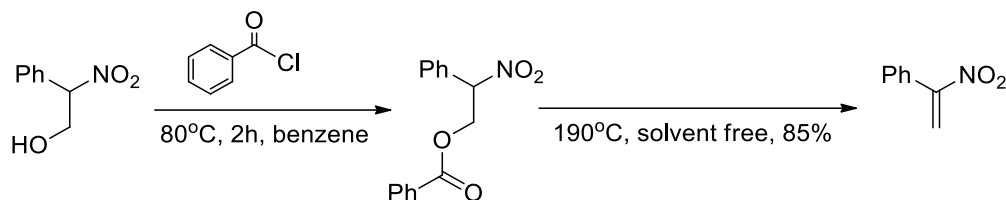


Fig. 9. Thermolysis of 2-benzoyloxy-1-phenyl-1-nitroethane leading to 1-phenyl-1-nitroethene.

According to similar procedure, the preparation of other nitroalkenes, such as 2-nitroprop-1-ene [44] is also possible.

Nitro-alkyl carboxylates can be prepared within independent preparative step, or, in some cases directly in the course of the synthesis of target compound. For example, phthalic anhydride melted with 2-nitroethanol is converted to the phthalic ester of the nitroalcohol. This ester, under reaction condition eliminate the molecule of phthalic acid which yield the free nitroethene [45] (Fig.10.).

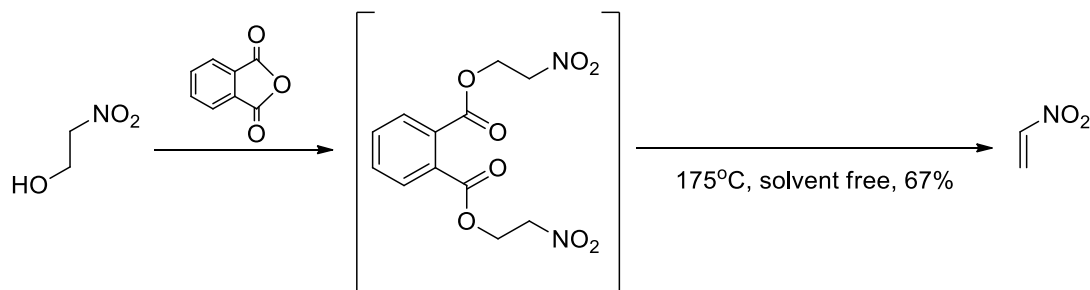


Fig. 10. Synthesis of the nitroethene via decomposition of the phthalic ester of 2-nitroethanol.

On the similar way, some substituted nitro-ethenes can be also prepared – such as 2-nitroprop-1-ene, 1-nitroprop-1-ene [45], 2-nitrobut-1-ene [46], 2-nitrobut-2-ene [47], 2-nitro-3-methyl-but-1-ene [43] and other. For these-type transformations, the “concerted” (“pericyclic”) mechanism was proposed a long term ago. The last discoveries in the framework of the Molecular Electron Density Theory [48] shows that the carboxylic acids extrusion are realized via other one step, multi-stage mechanism [49-51].

The elimination of carboxylic acids, under relatively milder conditions is possible in the presence of the inorganic bases. However, the reaction mechanism dramatically

changed. All these-type transformation are realised via stepwise E1<sub>cb</sub> mechanism, instead of one-step mechanism observed under non-catalytic conditions. For example, 2-fluor-2-nitroethyl acetate decompose in the presence of sodium acetate to 1-fluor-1-nitroethene at 130°C [52] (Fig.11.).

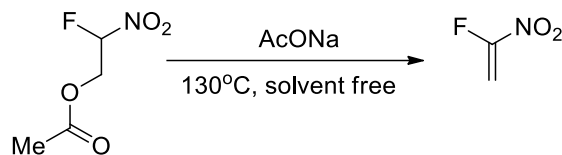


Fig. 11. Decomposition of 2-fluor-2-nitroethyl acetate.

For the comparison, all attempts for the obtaining the 1-bromo-1-nitroethene in similar way were not successful [32].

Analogous transformations with the participation of largest molecules proceed under milder conditions. For example, 3,3,3-trichloro-1-nitroprop-1-ene can be prepared during the heating in the boiling benzene solution of respective ester [53] (Fig.12.). Similar methodology can be applied for the preparation of very rare 3,3,3-tribromo-1-nitroprop-1-ene [54].

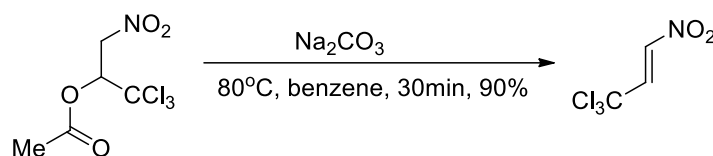


Fig. 12. Decomposition of the 1,1,1-trichloro-2-acetoxy-3-nitropropane.

In the last years, the possibility of the carboxylic acid's extrusion in the environment of ionic liquids was explored using DFT techniques. It was found, that these type transformations are possible under relatively mild conditions [55-57]. What is interesting, in the case of the reaction in the presence of triethylammonium cations, the stepwise ionic mechanism is enforced instead of polar one-step mechanism [55].

It should be mentioned, that not only nitro-alkyl carboxylates can be applied for the synthesis of conjugated nitroalkenes. This is possible also based on esters of mineral acids. For example, 2-chloro-2-nitroethyl nitrate decompose at 170°C yielded 1-chloro-1-nitroethene [58] (Fig.13.).

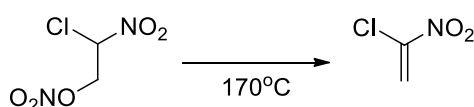


Fig. 13. Decomposition of 2-chloro-2-nitroethyl nitrate leading to 1-chloro-1-nitroethene.

Dehydrohalogenation

Some nitroalkenes can be prepared via non-catalysed HX extrusion. These type processes require rather high temperature. For example, 2-chloro-1-nitroethane in the gas phase decompose at 400°C (!) to nitro-ethene (Fig.14.). In this case, reaction yield is only 30% [59].

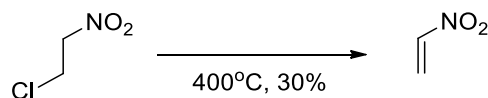


Fig. 14. Gaseous phase 2-chloro-1-nitroethane decomposition into nitroethene.

On the other hand, the introduction of base catalyst for the reaction environment stimulate rather mild conditions of dehydrohalogenation of 2-halo-1-nitroparaffins. Under catalytic conditions, the one step or stepwise biradical mechanism, is replaced to the stepwise E1CB-like mechanism. This strategy was applied inter alia for the synthesis of 2-phenyl-1-bromo-1-nitroethene [60] (Fig.15.). For example, it was found, that the elimination of HBr from the 1,2-dibromo-1-nitro-2-phenylethane is realized in the presence of the pyridine within very short time with 82% yield.

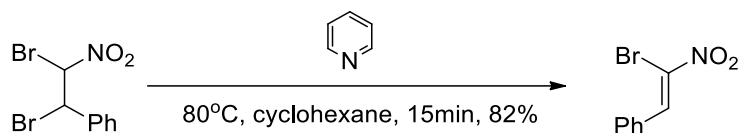


Fig. 15. Elimination of HBr leading to 2-phenyl-1-bromo-1-nitroethene.

Similar synthesis of 3,3,3-trichloro-1-bromo-1-nitroprop-1-ene is realized at room temperature in the catalytic presence of picoline (Fig.16.) [61].

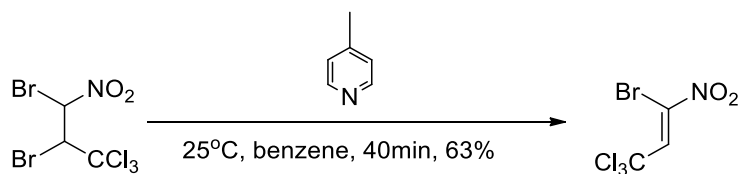


Fig. 16. Synthesis of 3,3,3-trichloro-1-bromo-1-nitroprop-1-ene realized in the catalytic presence of picoline.

The elimination of HCl from saturated chloro-nitro compounds is also possible in the suspension of the anhydrous sodium acetate in non-polar environment. On this way, a series of 2-EWG-1-nitroethenes can be prepared [62-63]. For example, methyl 3-nitro-2-chloronitroprop-1-enoate is decomposed at low temperature in the diethyl ether solution with the yield higher than 90% (Fig.17.).

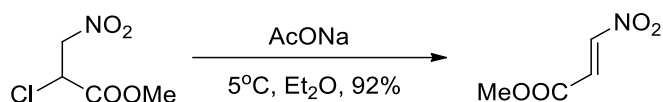


Fig. 17. Elimination of HCl from the methyl 3-nitro-2-chloronitroprop-1-enoate.

Less known, but also applied are processes on the basis of HI extrusion [64-65].

### Deamination

The direct deamination processes are not attractive in the application of synthesis of conjugated nitroalkenes, because amino or alkylamino moieties are not good leaving groups [66]. In the consequence, the preparation of conjugated nitroalkenes on this way lead with very low yields [67]. Better results can be obtained via the pyrolysis of respective ammonium salts. For example, N-(2-nitroamyl)-diethyl-amine can easily be converted to respective hydrochloride, and further to 2-nitropent-1-ene via pyrolysis stage (Fig.18.).

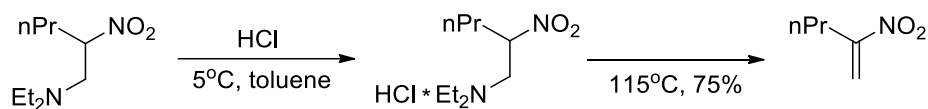


Fig. 18. Multistep conversion of N-(2-nitroamyl)-diethyl-amine to 2-nitropent-1-ene.

Similar transformations are also possible based on respective boron trifluoride complexes. These transformations require slightly lower temperatures and give expected products with satisfactory yields. The example is the preparation of 2-nitrobut-1-ene [68] (Fig.19.).

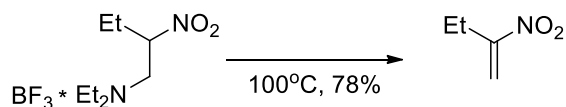


Fig. 19. Synthesis of 2-nitrobut-1-ene from boron trifluoride complexes.

It should be underlined at this point, that this synthetic strategy is adequate only for the preparation of alkyl functionalized nitro-ethenes.

### Other processes

For some, rather rare nitroalkenes, specific methodologies should be applied. This situation is observed in the case of poly nitro substituted alkenes. For example, only one synthetic protocol for the preparation of 1,2-dinitroethene is known. This procedure is based on the 1,2-dinitroethane, which can be converted in to respective disodium nitronate. Next, the obtained nitronate is treated with cold bromine, which lead directly to relatively stable 1,2-dinitroethene [69] (Fig.20.).



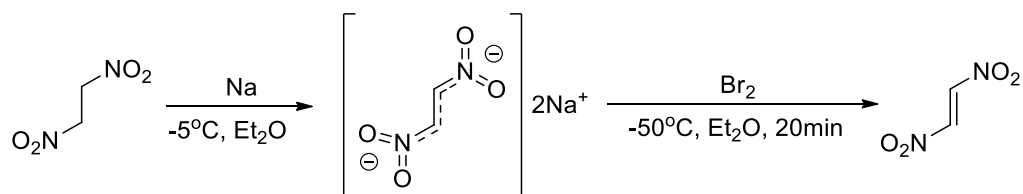


Fig. 20. Synthesis of 1,2-dinitroethene on the basis of the 1,2-dinitroethane.

For the preparation of tetranitroethene, the pyrolysis of hexanitroethane can be applied. This process is realized at 260°C and lead to relatively stable nitroalkene (Fig.21).

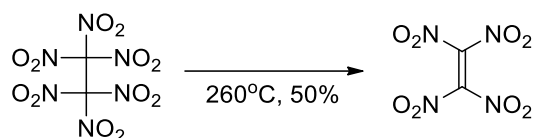


Fig. 21. Pyrolysis of the hexanitroethane.

## Conclusions

The preparation of conjugated nitroalkenes is a subject of the intensive exploration starting from the first part of the XX century. At the present time, many different strategies for the preparation of conjugated nitroalkenes are known. These approaches exhibit substantially different value. For example, interactions of alkenes with nitrating agents lead to mixtures of many, difficult for the separation nitro compounds as well as esters of nitrous acid. The elimination of small inorganic or organic molecules from saturated nitro-compounds open a wide range of possibility of the selective preparation of target molecular systems. For this purpose, different strategies such as dehydration, dehydrohalogenation or carboxylic acids extrusion can be applied. The last group of processes attracts especially attention, due to the relatively mild conditions, excellent yields and the relatively broadest range of potential applications.

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