

Recent progress in the field of cycloaddition reactions involving conjugated nitroalkenes

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ABSTRACT

In this review we present recent progress in the cycloaddition reactions of conjugated nitroalkenes with alkenes, conjugated 1,3-dienes or three atoms components (eg. nitrones, azides, diazocompounds, azomethine imines and ylides).

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1. Introduction

In recent decades, novel reactions based on conjugated nitroalkenes (CNA) as the key substrates have emerged and numerous challenging targets have been achieved. This was possible primarily due to the ease of preparation or ready availability and the diverse reactivity of nitroalkenes. Moreover, the presence of the nitro group allows to obtain bioactivity and useful building blocks for organic synthesis.^{1–3} Cycloadditions are one of the most important transformations in organic chemical synthesis and are a universal method of preparation of many heterocyclic compounds.^{4–10} This work is an attempt to synthetically discuss the results of research in the field of cycloadditions of conjugated nitroalkenes.

2. Cycloaddition reactions involving conjugated nitroalkenes

2.1. [2+2] Cycloaddition reactions

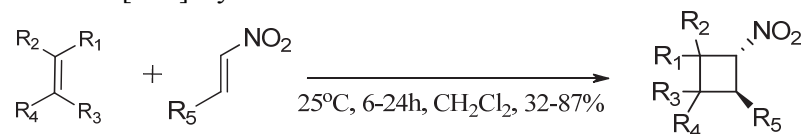
Mohr et al.¹¹ found that nitro-substituted cyclobutanes can be accessed by a visible-light-induced (at $\lambda=419\text{nm}$) [2+2] cycloaddition reaction involving various 2-arylnitroethenes. Authors found, that the larger excess of the olefine lead to higher product yields (37-87%) (see Table 1). The analysis of minor products and triplet sensitization experiments support a mechanistic scenario in which a 1,4-diradical is formed as a reaction intermediate.

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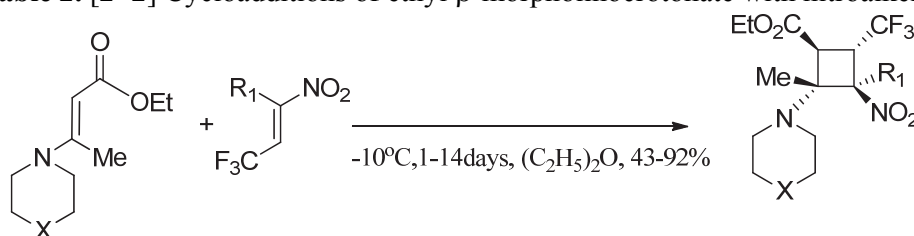
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Table 1. [2+2] Cycloadditions of olefins with nitroalkenes

Entry	Alkene	Nitroalkene	Yield [%]	Time	d.r.
1	R ₁ = indene	R ₅ =C ₆ H ₅	87	6–24 h	72:28
2	R ₁ =OCH ₂ CH ₃ , R ₂ = R ₃ = R ₄ =H	R ₅ =C ₆ H ₅	43	6–24 h	58:42
3	R ₁ = C ₆ H ₅ , R ₂ = CH ₃ , R ₃ = R ₄ =H	R ₅ =C ₆ H ₅	52	6–24 h	54:46
4	R ₁ = CH ₃ , R ₂ =C(CH ₂)(CH ₃), R ₃ = R ₄ =H	R ₅ =C ₆ H ₅	75	6–24 h	51:49
5	R ₁ =R ₂ = R ₃ = R ₄ = CH ₃	R ₅ =C ₆ H ₅	59	6–24 h	
6	2,3-dihydrofuran	R ₅ =C ₆ H ₅	36	6–24 h	
7	methylenecyclohexane	R ₅ =C ₆ H ₅	51	6–24 h	
8	cyclopentene	R ₅ =C ₆ H ₅	57 ^a	24h	87:13
9	R ₁ =R ₂ = R ₃ = R ₄ = CH ₃	R ₅ =4-CH ₃ -C ₆ H ₄	54	2–4 h	
10	R ₁ =R ₂ = R ₃ = R ₄ = CH ₃	R ₅ =4-OCH ₃ -C ₆ H ₄	52	2–4 h	
11	R ₁ =R ₂ = R ₃ = R ₄ = CH ₃	R ₅ =4-CN-C ₆ H ₄	32	6 h	
12	R ₁ =R ₂ = R ₃ = R ₄ = CH ₃	R ₅ =2-thiophene	50	2–4 h	

^a)λ = 350 nm

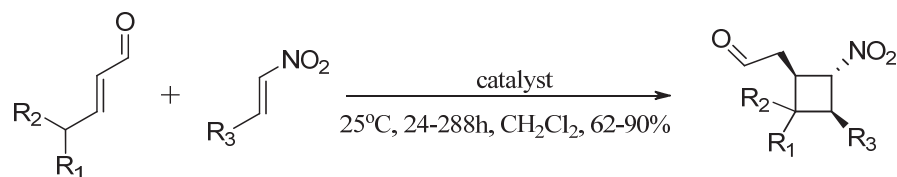
Sosnovskikh et al.¹² analyzed thermal [2+2] cycloaddition reactions of (E)-3,3,3-trifluoro-1-nitropropene with ethyl β-morpholinocrotonate. They give a cyclobutane derivative as the product, but it was more rarely alternative to Diels-Alder reaction (Table 2).

Table 2. [2+2] Cycloadditions of ethyl β-morpholinocrotonate with nitroalkenes

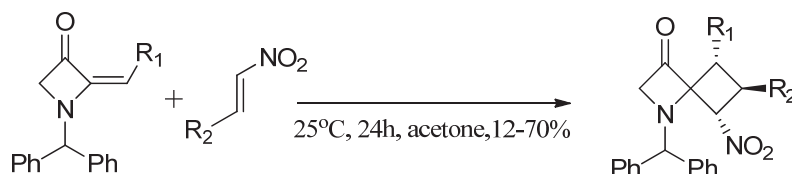
Entry	Alkene	Nitroalkene	Yield [%]	Time
1	X=CH ₂	R ₁ =H	90	45 min
2	X=O	R ₁ =H	92	24h
3	X=CH ₂	R ₁ =CH ₃	43	12–14 days

Jørgensen et al.¹³ described reaction of 2-phenylnitroethene with α,β-unsaturated aldehydes. Through use of the bifunctional squaramide catalyst ((S)-3-(3,5-bis(trifluoromethyl)phenylamino)-4-(pyrrolidin-2-ylmethylamino)cyclobut-3-ene-1,2-dione), they were able to generate the fully substituted cyclobutane products with excellent diastereo- and enantioselectivity (Table 3).

Soós et al.¹⁴ strained, captodative benzylidene-azetidinones are demonstrated to function as potent reaction partners in thermal [2+2] cycloaddition reactions with nitroalkenes. This reaction can be used to simplify the synthesis of aza-spiro[3.3]heptanes. The optimal solvent was the acetone, reactions were carried out for 24h in room temperature with Schreiner's catalyst (1,3-bis[3,5-bis(trifluoromethyl)phenyl]urea). The scope of olefins that can be reacted in [2+2] cycloaddition reactions is illustrated in Table 4.

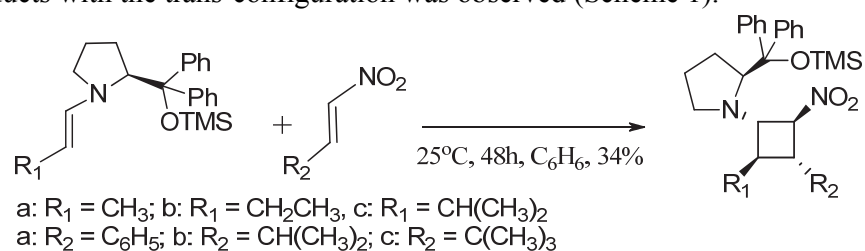
Table 3. [2+2] Cycloadditions of α,β -unsaturated aldehydes with nitroalkenes

Entry	Alkene	Nitroalkene	Time [h]	Yield [%]	d.r.
1	R ₁ =C ₆ H ₅ , R ₂ =H	R ₃ =C ₆ H ₅	24	86	>20:1
2	R ₁ =C ₆ H ₅	R ₃ =C ₆ H ₅	72	84	>20:1
3	R ₁ =C ₆ H ₅	R ₃ =C ₆ H ₅	288	81	>20:1
4	R ₁ =C ₆ H ₅	R ₃ =4-F-C ₆ H ₄	48	90	>20:1
5	R ₁ =C ₆ H ₅	R ₃ =4-Br-C ₆ H ₄	24	84	>20:1
6	R ₁ =C ₆ H ₅	R ₃ =2-Cl-C ₆ H ₄	48	80	>20:1
7	R ₁ =C ₆ H ₅	R ₃ =3-NO ₂ -C ₆ H ₄	32	82	>20:1
8	R ₁ =C ₆ H ₅	R ₃ =4-CH ₃ -C ₆ H ₄	48	84	>20:1
9	R ₁ =C ₆ H ₅	R ₃ =4-CH ₃ O-C ₆ H ₄	72	80	>20:1
10	R ₁ =C ₆ H ₅	R ₃ =2,6-Cl ₂ -C ₆ H ₃	48	87	>20:1
11	R ₁ =C ₆ H ₅	R ₃ =2,5-(CH ₃ O) ₂ -C ₆ H ₃	40	83	>20:1
12	R ₁ =C ₆ H ₅	R ₃ =2-furyl	48	74	>20:1
13	R ₁ =C ₆ H ₅	R ₃ =n-Bu	24	62	>20:1
14	R ₁ =2-CH ₃ C ₆ H ₄ , R ₂ =H	R ₃ =C ₆ H ₅	40	82	>20:1
15	R ₁ =1,3-benzodioxole, R ₂ =H	R ₃ =C ₆ H ₅	24	85	>20:1
16	R ₁ =3,5-(OCH ₃) ₂ -C ₆ H ₄ , R ₂ =H	R ₃ =C ₆ H ₅	24	93	>20:1
17	R ₁ =3-CF ₃ -C ₆ H ₄ , R ₂ =H	R ₃ =C ₆ H ₅	22	82	>20:1
18	R ₁ =R ₂ =CH ₃	R ₃ =C ₆ H ₅	72	71	>20:1

Table 4. [2+2] Cycloadditions of benzylidene-azetidinones with nitroalkenes

Entry	Alkene	Nitroalkene	Yield [%]	d.r.
1	R ₁ =C ₆ H ₅	R ₂ =4-Cl-C ₆ H ₄	75	9:1
2	R ₁ =2-Cl-C ₆ H ₄	R ₂ =4-Cl-C ₆ H ₄	12	>20:1
3	R ₁ =3-Cl-C ₆ H ₄	R ₂ =4-Cl-C ₆ H ₄	18	5:1
4	R ₁ =4-Cl-C ₆ H ₄	R ₂ =4-Cl-C ₆ H ₄	38	>20:1
5	R ₁ =4-Br-C ₆ H ₄	R ₂ =4-Cl-C ₆ H ₄	38	>20:1
6	R ₁ =2-OCH ₃ -C ₆ H ₄	R ₂ =4-Cl-C ₆ H ₄	43	>20:1
7	R ₁ =3-OCH ₃ -C ₆ H ₄	R ₂ =4-Cl-C ₆ H ₄	50	>20:1
8	R ₁ =4-OCH ₃ -C ₆ H ₄	R ₂ =4-Cl-C ₆ H ₄	65	>20:1
9	R ₁ =C ₆ H ₅	R ₂ =3-Cl-C ₆ H ₄	72	9:1
10	R ₁ =C ₆ H ₅	R ₂ =2-Cl-C ₆ H ₄	44	10:1
11	R ₁ =C ₆ H ₅	R ₂ =2,6-Cl ₂ -C ₆ H ₄	74	13:1
12	R ₁ =C ₆ H ₅	R ₂ =2-Cl,6-F-C ₆ H ₄	78	12:1
13	R ₁ =C ₆ H ₅	R ₂ =3,4-Cl ₂ -C ₆ H ₄	72	8:1
14	R ₁ =C ₆ H ₅	R ₂ =2-Br-C ₆ H ₄	37	>20:1
15	R ₁ =C ₆ H ₅	R ₂ =3-I-C ₆ H ₄	70	13:1
16	R ₁ =C ₆ H ₅	R ₂ =4-F-C ₆ H ₄	53	2:1
17	R ₁ =C ₆ H ₅	R ₂ =3,4,5-F ₃ -C ₆ H ₄	57	>20:1
18	R ₁ =C ₆ H ₅	R ₂ =4-OCH ₃ -C ₆ H ₄	30	7:1
19	R ₁ =C ₆ H ₅	R ₂ =3-OCH ₃ -C ₆ H ₄	67	12:1
20	R ₁ =C ₆ H ₅	R ₂ =3-OC ₂ H ₅ -C ₆ H ₄	76	>20:1
21	R ₁ =C ₆ H ₅	2-OCH ₃ -C ₆ H ₄	32	1.5:1
22	R ₁ =C ₆ H ₅	R ₂ =2-C≡C	50	>20:1
23	R ₁ =C ₆ H ₅	R ₂ =naftalene	44	>20:1
24	R ₁ =C ₆ H ₅	R ₂ =3-CH ₃ -C ₆ H ₄	55	12:1
25	R ₁ =C ₆ H ₅	R ₂ =4-CH ₂ CH ₃ -C ₆ H ₄	36	10:1
26	R ₁ =C ₆ H ₅	R ₂ =4-NO ₂ -C ₆ H ₄	33	3:1
27	R ₁ =C ₆ H ₅	R ₂ =2,4-(CF ₃) ₂ -C ₆ H ₄	64	>20:1
28	R ₁ =C ₆ H ₅	R ₂ =2-furane	33	5:1
29	R ₁ =C ₆ H ₅	R ₂ =2-thiophene	38	10:1
30	R ₁ =C ₆ H ₅	R ₂ =CH ₃	70	1:1
31	R ₁ =C ₆ H ₅	R ₂ =2-propane	27	>20:1
32	R ₁ =C ₆ H ₅	R ₂ =cycloheksane	31	>20:1

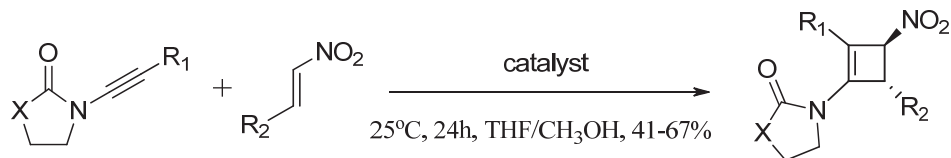
Hayashi et al.¹⁵ discovered that in reactions of 2-alkylnitroethenes with diphenylprolinol silyl ether-derived enamine in dry benzene, respective cyclobutanes was spontaneous and very fast formed. In all cases cycloadducts with the trans-configuration was observed (Scheme 1).



Scheme 1. [2+2] Cycloadditions of 2-alkylnitroethenes with diphenylprolinol silyl ether-derived enamine

Lam et al.¹⁶ reported the first, metal catalyzed [2+2] cycloaddition reactions of ynamides with 2-arylsubstituted nitroethenes, resulting in a range of cyclobutenamide products. The reactions are promoted by substoichiometric quantities of a racemic chiral diene–rhodium complex in conjunction with NaBPh₄ (Table 5).

Table 5. [2+2] Cycloadditions of ynamides with nitroalkenes.

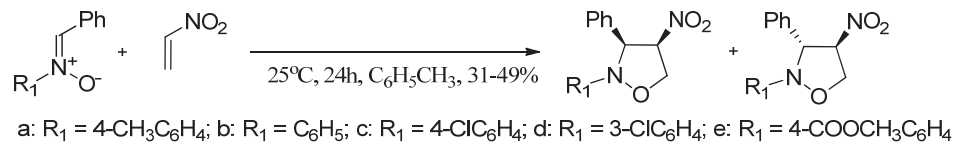


Entry	Alkyne	Nitroalkene	Yield [%]	d.r.
1	R ₁ =C ₆ H ₅ , X=O	R ₂ =C ₆ H ₅	60	87:13
2	R ₁ =4-F C ₆ H ₄ , X=O	R ₂ =C ₆ H ₅	59	81:19
3	R ₁ =4-CH ₃ O C ₆ H ₄ , X=O	R ₂ =C ₆ H ₅	55	87:13
4	R ₁ =3-NO ₂ C ₆ H ₄ , X=O	R ₂ =C ₆ H ₅	48	81:19
5	R ₁ =n-Hex, X=O	R ₂ =C ₆ H ₅	77	85:15
6	R ₁ =CH ₂ CH ₂ C ₆ H ₅ , X=O	R ₂ =C ₆ H ₅	59	87:13
7	R ₁ =CH ₂ CH ₂ OTBS, X=O	R ₂ =C ₆ H ₅	63	84:16
8	R ₁ =C ₆ H ₅ , X=CH ₃ N	R ₂ =C ₆ H ₅	55	89:11
9	R ₁ =C ₆ H ₅ , X=CH ₂	R ₂ =C ₆ H ₅	62	87:13
10	R ₁ =CH ₂ CH ₂ C ₆ H ₅ , X=CH ₂	R ₂ =C ₆ H ₅	41	82:18
11	R ₁ =C ₆ H ₅ , X=O	R ₂ =naftalene	47	82:18
12	R ₁ =C ₆ H ₅ , X=O	R ₂ =4-F C ₆ H ₄	67	82:18
13	R ₁ =C ₆ H ₅ , X=O	R ₂ =4-Br C ₆ H ₄	66	84:16
14	R ₁ =C ₆ H ₅ , X=O	R ₂ =4-NO ₂ C ₆ H ₄	67	86:14

2.2 [3+2] Cycloaddition

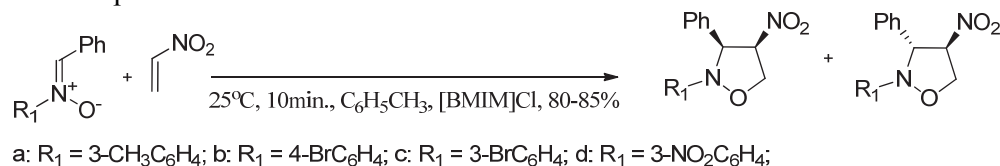
Predominantly, in [3+2] cycloaddition reactions involving CNAs, three atoms components of allylic type is most often used. To the most popular processes can include reaction using by nitrones.

The most commonly used CNAs, in reaction with nitrones, is nitroethene. For example, Jasiński¹⁷ carried out series of [3+2] cycloaddition reactions of nitroethene to (Z)-N-aryl-C-phenylnitrones, which lead to mixtures of stereoisomeric 3,4-*cis*- and 3,4-*trans*-2-aryl-4-nitro-3-phenylisoxazolidines (Scheme 2). The processes are realized at room temperature, in the dark, and using by dry toluene as a solvent. The conversion of substrates was about 24 hours.



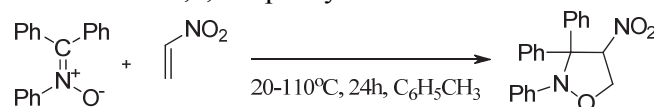
Scheme 2. [3+2] cycloaddition reactions of nitroethene to (Z)-N-aryl-C-phenylnitrones.

The similar reactions were realized in ionic liquid as a solvent. Processes are realized using by 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) at room temperature gave mixtures of 3,4-*cis*- and 3,4-*trans*-2-aryl-3-phenyl-4-nitroisoxazolidines with 80-85% yields (Scheme 3). It should be underlined, that the application of an ionic liquid allows to shorten the conversion time of substrates to 10 minutes in comparison to toluene solution¹⁸.



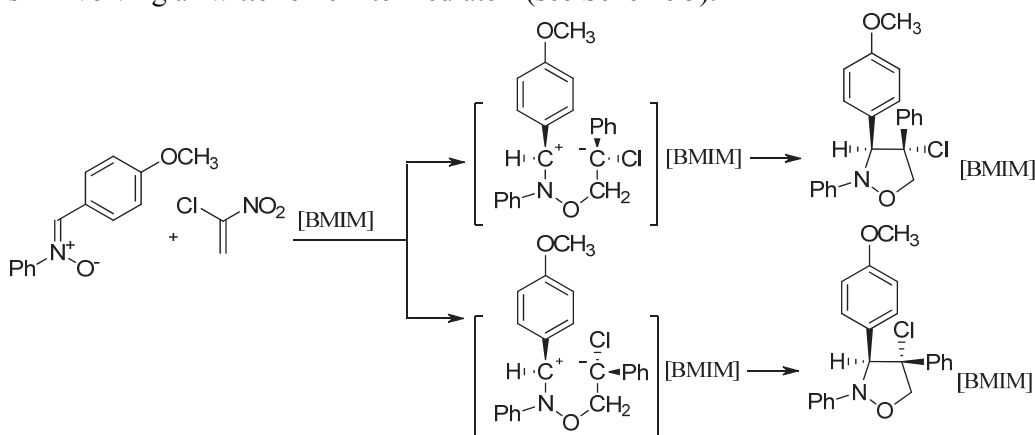
Scheme 3. [3+2] cycloaddition reactions of nitroethene to (Z)-N-aryl-C-phenylnitrones in ionic liquid.

Jasiński¹⁹ also carried out [3+2] cycloaddition reactions of C,C,N-triphenylnitronium to nitroethene (Scheme 4). It was reported that, in the contrast to earlier reports²⁰, the process is full regioselectively independently of the temperature. In particularly at room temperature and in 110°C, a course of reaction is formed only one product – 4-nitro-2,3,3-triphenylisoxazolidine.



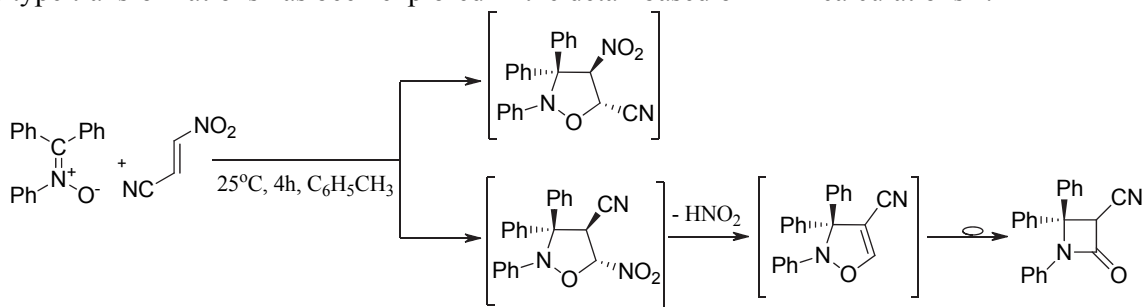
Scheme 4. [3+2] cycloaddition reactions of C,C,N-triphenylnitronium to nitroethene.

The DFT calculations explained, the source of high efficiency of reactions between nitroalkenes and nitrones in ionic liquids. In particular, [3+2] cycloaddition reaction between *gem*-chloronitroethene and (Z)-C-4-methoxyphenyl-N-phenylnitronium in the presence of [BMIM] cations proceed via two-step mechanism involving a zwitterionic intermediate²¹ (see Scheme 5).



Scheme 5. [3+2] cycloaddition reaction between *gem*-chloronitroethene and (Z)-C-4-methoxyphenyl-N-phenylnitronium.

Other types of substituted nitroethenes are also often used in reactions with nitrones. An example is cycloaddition of triphenylnitronone with 2-cyanonitroethene (Scheme 6). The process does not lead to the stable products. Primary formed 4-nitroisoxazolidine decomposed easily to substrates, while 5-nitroisoxazolidine is converted to β -lactam. The processes were realized at room temperature, and using dry toluene as a solvent. The conversion of substrates was about 4 hours²². Mechanistic aspects of this type transformations has been explored in the detail based on DFT calculations²⁰.



Scheme 6. [3+2] cycloaddition of triphenylnitronone with 2-cyanonitroethene.

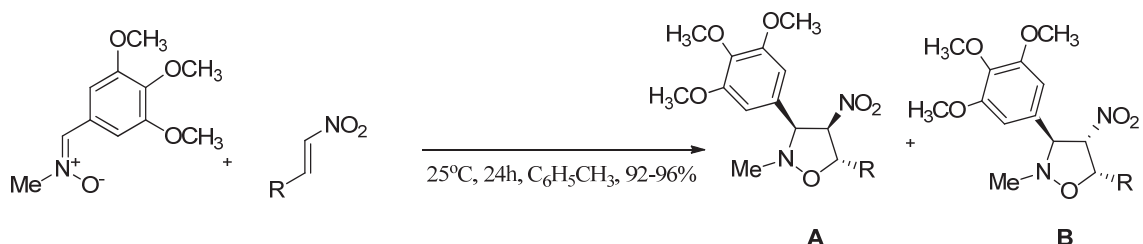
Bigotti *et al.*²³ carried out the reaction with the participation of γ -fluoro- α -nitroalkenes in the [3+2] cycloaddition reactions with nitrones. These reactions leads to isoxazolidines in good to excellent yields, with total regiocontrol and nearly complete diastereocontrol in favor of the isomers with 3,4-cis configuration (Table 6). All processes are realized in mild condition.

Table 6. Reaction between γ -fluoro- α -nitroalkenes and nitrones

Entry	Nitronone	Nitroalkene	Yield [%]	d.r.
1	$R_1=R_2=C_6H_5$	$R_2=CF_3$	85	3:1
2	$R_1=R_2=C_6H_5$	$R_2=CF_2Cl$	85	4:1
3	$R_1=R_2=C_6H_5$	$R_2=CF_2H$	87	2:1
4	$R_1=R_2=C_6H_5$	$R_2=CF_2CF_2$	76	1:1
5	$R_1=CH_3, R_2=C_6H_5$	$R_2=CF_3$	83	4:1
6	$R_1=CH_3, R_2=C_6H_5$	$R_2=CF_2Cl$	93	8:1
7	$R_1=$ naftalene, $R_2=CH_2C_6H_4$	$R_2=CF_3$	84	1:1
8	$R_1=$ naftalene, $R_2=CH_2C_6H_4$	$R_2=CF_2Cl$	78	4:3
9	$R_1=$ naftalene, $R_2=CH_2C_6H_4$	$R_2=CF_2H$	81	1:1
10	$R_1=$ naftalene, $R_2=CH_2C_6H_4$	$R_2=CF_2CF_2$	65	1:1
11		$R_2=CF_3$	52	2:1
12		$R_2=CF_2Cl$	61	1:1
13		$R_2=CF_2H$	45	2:1
14		$R_2=CF_2CF_2$	48	3:1
15		$R_2=CF_3$	83	4:1
16		$R_2=CF_2Cl$	93	8:1
17	$R_1=CH_2C_6H_4, R_2=H$	$R_2=CF_3$	75	
18	$R_1=CH_2C_6H_4$	$R_2=CF_2Cl$	88	
19	$R_1=CH_2C_6H_4$	$R_2=CF_2H$	74	
20	$R_1=CH_2C_6H_4$	$R_2=CF_2CF_2$	73	

Properly 2-substituted nitroethenes are used in series of [3+2] cycloaddition reaction with (Z)-C-(3,4,5-trimethoxyphenyl)-N-methylnitron as three atoms component. The authors show that these type of processes are a regioselective and a stereoselective. The processes are realized at room temperature, in the dark, and using by dry toluene as a solvent. The conversion of substrates was about 24 hours²⁴ (Table 7).

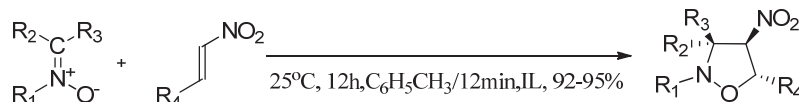
Table 7. Reaction between properly 2-substituted of nitroethene and (Z)-C-(3,4,5-trimethoxyphenyl)-N-methylnitron

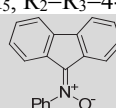


Entry	Nitroalkene	Yield [%]	Products A : B
1	R=CH ₃	96	80:14
2	R=CH ₂ CH ₂ CH ₃	94	73:17
3	R=CCl ₃	92	67:30

New 2,3,3,5-tetra-substituted-4-nitroisoxazolidines may be synthesized in a reaction between ketonitrones and 2-EWG-nitroethenes. The processes are realised both in toluene and also in ([BMIM]Cl). Authors show that all of these type [3+2] cycloaddition reactions are realised in mild condition with complete regioselectivity, and lead with high yields to sterically crowded products²⁵ (Table 8). Kinetic studies indicate that all these cycloadditions do take place according to a mechanism that proceeds without intervention of zwitterionic intermediate²⁶.

Table 8. Reaction between (E)-3,3,3-trichloro-1-nitroprop-1-ene and (Z)-C-diphenyl-N-arylnitron

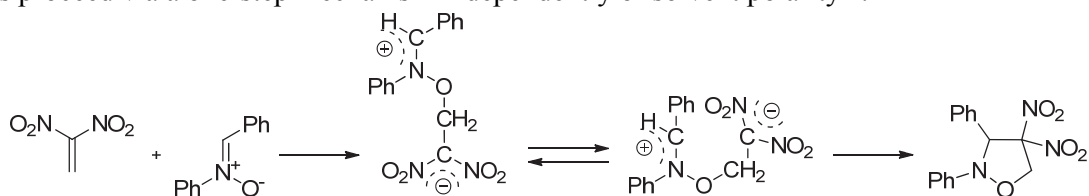


Entry	Nitron	Alkene	Yield [%]
1	R ₁ = C ₆ H ₅	R ₄ = CCl ₃	95 ^a , 94 ^b
2	R ₁ = 4-OCH ₃ C ₆ H ₄	R ₄ = CCl ₃	94 ^a , 92 ^b
3	R ₁ = 4-BrC ₆ H ₄	R ₄ = CCl ₃	95 ^a , 93 ^b
4	R ₁ = C ₆ H ₅ , R ₂ = R ₃ = 4-CH ₃ C ₆ H ₄	R ₄ = CCl ₃	98 ^a
5		R ₄ = CCl ₃	96 ^a
6	R ₁ = R ₂ = R ₃ = C ₆ H ₅	R ₄ = COOCH ₃	91 ^a

^atoluene, 12h
^bIL, 45min

In recent time, gem-1,1-dinitroethene became the object of research as a highly reactive and useful π -deficient three atoms components. The DFT calculations showed the clearly polar nature of [3+2] cycloaddition reaction between gem-dinitroethene and (Z)-C,N-diphenylnitron (Scheme 7). The course of reaction leading to 2,3-diphenyl-4,4-dinitroisoxazolidine is kinetically favoured. Authors showed that depending on the reaction environment polarity, the process can lead according to different mechanisms. The conducting the reaction in the gas phase causes the product of [3+2] cycloaddition

reaction to be formed in accordance with the one-step mechanism. When the reaction is conducted in toluene, the reaction proceeds according via zwitterionic stepwise scheme²⁷. It should be underlined, that [3+2] cycloaddition reactions of the same gem-1,1-dinitroethene to different type of nitrile N-oxides proceed via a one-step mechanism independently of solvent polarity²⁸.

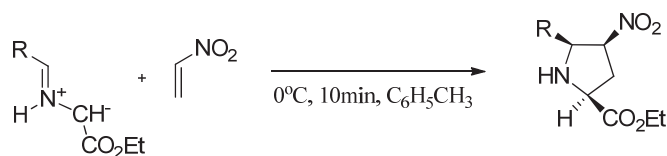


Scheme 7. [3+2] cycloaddition reaction between gem-dinitroethene and (Z)-C,N-diphenylnitrone

Another three atoms components allylic type which is used in reaction with CNA is azomethineylide, both acyclic, and cyclic compounds.

*Nyerges et al.*²⁹ carried out a series of reactions between nitroethene and *in situ* generated azomethineylides as three atoms components. These processes are carried out in dry toluene, at 0°C and in the presence of silver acetate. The [3+2] cycloaddition reactions gave the expected pyrrolidine in all cases (Table 9).

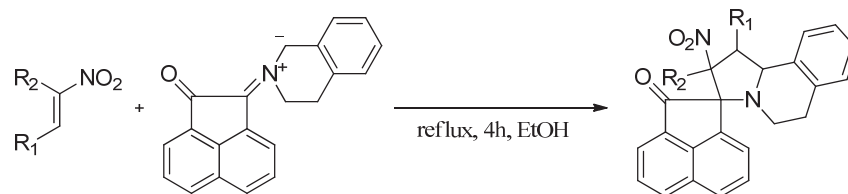
Table 9. Reaction between nitroethene and azomethineylide



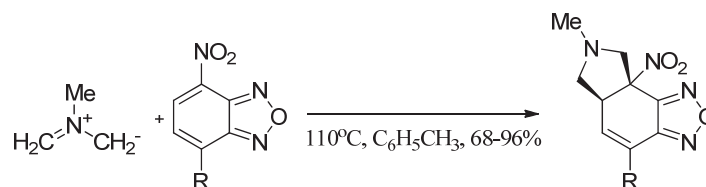
Entry	Azomethineylide	Yield [%]
1	R=C ₆ H ₅	44
2	R=4-OCH ₃ C ₆ H ₄	56
3	R=2,4-Cl ₂ C ₆ H ₃	64
4	R=4-OCH ₃ C ₆ H ₄	54
5	R=4-ClC ₆ H ₄	55
6	R=4-CF ₃ C ₆ H ₄	62
7	R=2-CH ₃ C ₆ H ₄	58
8	R=2,3-(OCH ₃) ₂ C ₆ H ₃	54
9	R=2-NO ₂ C ₆ H ₄	35

*Sarrafî et al.*³⁰ prepared spiroacenaphthene pyrroloisoquinoline in series, using various 12 arylnitroethenes as a CNAs. Products were formed with full regioselectivity. The process are realized in ethanol as a solvent and reflux. Conversion of substrates is about 4 hours (Table 10).

*Starosotnikov et al.*³¹ carried out a series of reactions based on the [3+2] cycloaddition reactions of N-methylazomethine ylide with substituted 4-nitrobenzofurazanes. In a courses of reactions only one of two possible products are formed. Also Authors observed that the cycloaddition process was found to be affected by substituents in the benzene ring.

Table 10. Reaction between nitroethene and azomethineylide

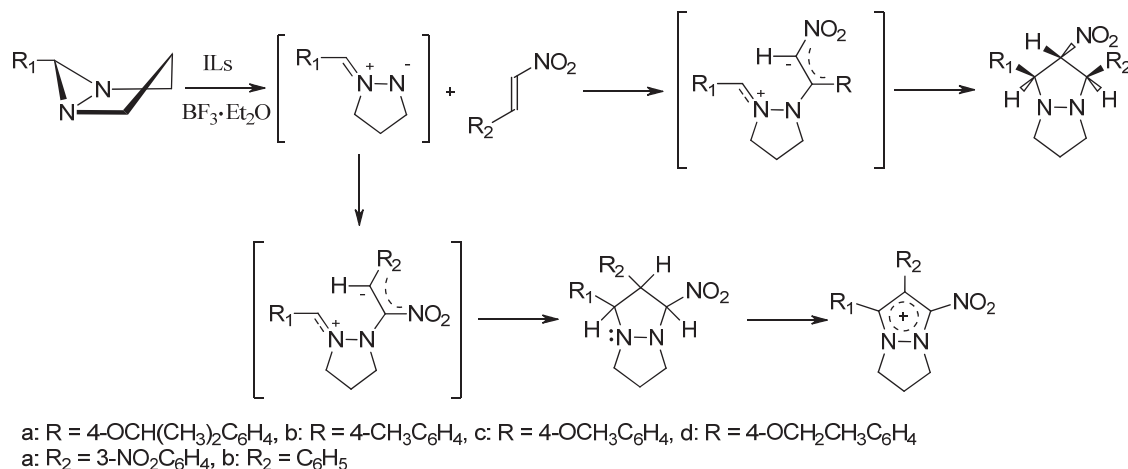
Entry	Nitroalkene	Yield [%]
1	R ₁ =C ₆ H ₅ , R ₂ =H	83
2	R ₁ =4-FC ₆ H ₄ , R ₂ =H	81
3	R ₁ =4-ClC ₆ H ₄ , R ₂ =H	76
4	R ₁ =4-BrC ₆ H ₄ , R ₂ =H	78
5	R ₁ =4-CH ₃ C ₆ H ₄ , R ₂ =H	78
6	R ₁ =4-OCH ₃ C ₆ H ₄ , R ₂ =H	81
7	R ₁ =3-OCH ₃ C ₆ H ₄ , R ₂ =H	78
8	R ₁ =4-NCH ₃ C ₆ H ₄ , R ₂ =H	81
9	R ₁ =4-OCH ₃ C ₆ H ₄ , R ₂ =H	78
10	R ₁ =4-NO ₂ C ₆ H ₄ , R ₂ =H	82
11	R ₁ =2-Cl-5-NO ₂ C ₆ H ₄ , R ₂ =H	80
12	R ₁ =C ₆ H ₅ , R ₂ =CH ₃	80

Table 11. Reaction between N-methylazomethineylide and 4-nitrobenzofurazans

4-nitrobenzofurazane	Time [min]	Yield [%]
R=SC ₆ H ₄	10	68
R=OCH ₃	40	87
R=CH ₂ -S C ₆ H ₄	15	96
R=OC ₆ H ₄	15	90
R=N-(CH ₂) ₅	-	-
R=NHC ₆ H ₄	-	-
R=2-(COOCH ₃)C ₄ H ₇ -N	-	-

Much less often reactions with the participation of azomethine imines and thiocarbonylides were carried out.

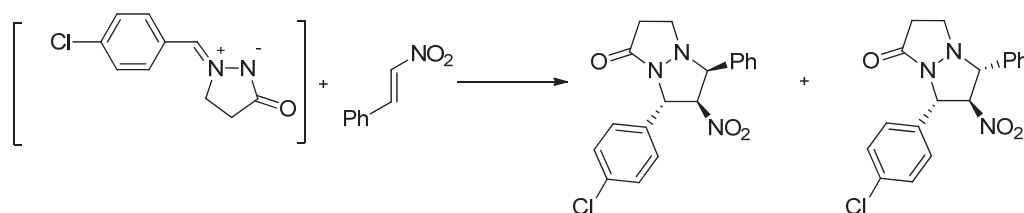
Makhova et al.³² carried out the reactions 1-nitro-2-(3-nitrophenyl)-ethylene with 6-aryl-1,5-diazabicyclo[3.1.0]hexanes in ionic liquids (ILs) [BMIM][BF₄] and [BMIM][PF₆] (see Scheme 8). To generate azomethine imines, to the reaction mixture was added BF₃·Et₂O in order to break the diaziridine ring. It could be expected that the addition of β-nitrostyrenes to three atoms components should run via the *Michael addition* pathway through intermediates generating 1,3-diaryl-2-nitrotetrahydro-1H,5H-pyrazolo[1,2-a]pyrazoles. The processes are realized at room temperature or with moderate heating. Expected products were obtained in all the cases. However, apart from them, tetrafluoroborates of 5,6-diaryl-2,3-dihydro-1H-pyrazolo[1,2-a]pyrazolium and hexafluorophosphate of 5,6-diaryl-2,3-dihydro-1H-pyrazolo[1,2-a]pyrazolium were unexpectedly isolated. Assumingly, compounds were formed as a result of the interaction of properly substituted β-nitrostyrene with three atoms components, contrary to the Michael addition mechanism, generating second intermediates.



Scheme 8. Reactions 1-nitro-2-(3-nitrophenyl)-ethylene with 6-aryl-1,5-diazabicyclo[3.1.0]hexanes in ionic liquids

Yang and Fan³³ carried out a series of reactions between azomethine imine system and 2-aryl-1-nitroethenes. The first, they examined the reaction of azomethine imine with properly substituted of 2-aryl-1-nitroethenes in different solvents. It was found that the reaction in most organic solvents at reflux, such as in chloroform, tetrahydrofuran, acetonitrile and methanol (with comparatively low boiling points), led to [3+2] cycloaddition reactions product in good yields in the absence of a catalyst (Table 12). If the reaction was carried out in a polar solvent, such as dimethyl sulfoxide, at 60°C, a trace amount of together with the normal product was formed. Further increasing the reaction temperature resulted in an increased yield of until almost it was the sole product at temperatures higher than 100°C. However, it was proved that temperature was not the only factor for this steric course, the same reaction was carried out at the same temperature (about 110°C) in toluene (as a nonpolar solvent). It was found that the yield of decreased markedly and was generated as the main product.

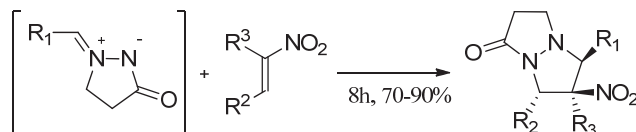
Table 12. Reaction of azomethine imine with properly substituted 2-aryl-1-nitroethenes in different solvents



Entry	Solvent	Temperature [°C]	Time [h]	Yield [%]
1	CHCl ₃	reflux	8	82
2	THF	reflux	8	78
3	Acetone	reflux	8	80
4	MeCN	reflux	8	73
5	MeOH	reflux	8	76
6	DMSO	60	48	60
7	DMSO	110	48	68
8	DMF	110	48	41
9	H ₂ O	reflux	48	38
10	toluene	reflux	48	73

Moreover, the authors also studied the course of the reaction using a series of various substituted azomethine imines and analogs of 2-aryl-1-nitroethenes. In a course of reaction are formed main one product. It seems that the reactions are tolerant to various substituted compounds. The substituent on the aromatic ring has no significant effect on this transformation (**Table 13**).

Table 13. Various substituted azomethine imines and analogs of 2-aryl-1-nitroethenes

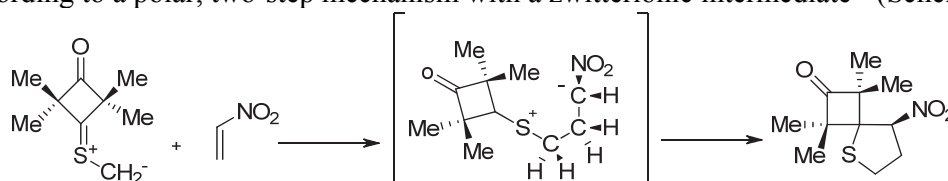


Entry	Azomethine imine	Nitroalkene	Yield [%]
1	R ₁ =C ₆ H ₅	R ₂ =4-ClC ₆ H ₄ , R ₃ =H	82 ^{a)} , 68 ^{b)}
2	R ₁ =C ₆ H ₅	R ₂ =4-BrC ₆ H ₄ , R ₃ =H	79 ^{a)} , 62 ^{b)}
3	R ₁ =C ₆ H ₅	R ₂ =C ₆ H ₅ , R ₃ =H	84 ^{a)} , 55 ^{b)}
4	R ₁ =C ₆ H ₅	R ₂ =4-CH ₃ C ₆ H ₄ , R ₃ =H	87 ^{a)} , 54 ^{b)}
5	R ₁ =C ₆ H ₅	R ₂ =2,4-Cl ₂ C ₆ H ₃ , R ₃ =H	89 ^{a)} , 57 ^{b)}
6	R ₁ =4-ClC ₆ H ₄	R ₂ =C ₆ H ₅ , R ₃ =H	85 ^{a)} , 51 ^{b)}
7	R ₁ =4-ClC ₆ H ₄	R ₂ =4-ClC ₆ H ₄ , R ₃ =H	73 ^{a)} , 55 ^{b)}
8	R ₁ =4-CH ₃ C ₆ H ₄	R ₂ =4-ClC ₆ H ₄ , R ₃ =H	72 ^{a)} , 52 ^{b)}
9	R ₁ =4-OCH ₃ C ₆ H ₄	R ₂ =4-ClC ₆ H ₄ , R ₃ =H	82 ^{a)} , 53 ^{b)}
10	R ₁ =CH=CHC ₆ H ₅	R ₂ =C ₆ H ₅ , R ₃ =H	88 ^{a)} , 56 ^{b)}
11	R ₁ =CH=CHC ₆ H ₅	R ₂ =2,4-Cl ₂ C ₆ H ₃ , R ₃ =H	90 ^{a)} , 42 ^{b)}
12	R ₁ =CH=CHC ₆ H ₅	R ₂ =C ₆ H ₅ , R ₃ =CH ₃	70 ^{a)} , 24 ^{b)}

^{a)} 61°C, CHCl₃

^{b)} 110°C, DMSO

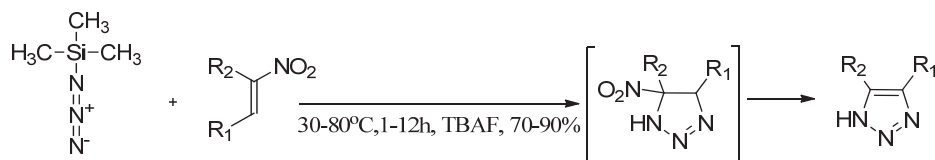
The use in reactions of thiocarbonylides as a three atoms component with conjugated nitroalkenes is known from theoretical considerations. DFT calculations, for various levels in theory, show that the reaction of 2,2,4,4-tetramethyl-3-thiocyclobutanone S-methylidewith nitroethene takes place according to a polar, two-step mechanism with a zwitterionic intermediate⁵⁹ (Scheme 9).



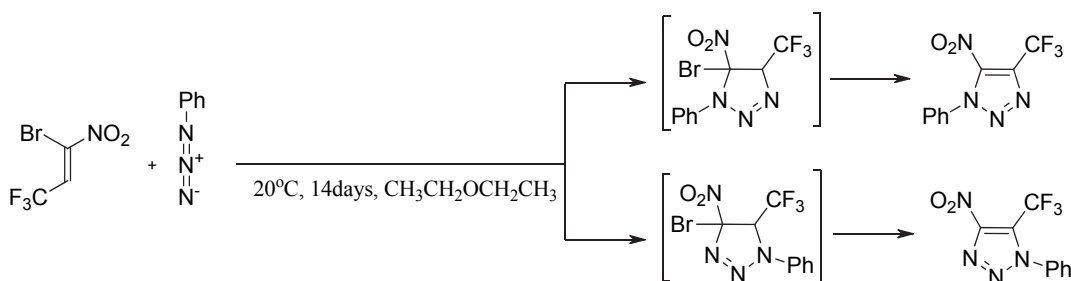
Scheme 9. Reactions of thiocarbonylides with conjugated nitroalkenes.

Definitely, allenic type three atoms components (such as azides, nitrile N-oxides and diazocompounds) is much less used in reaction with CNAs. So, *Fringuelli* and *Vaccaro*⁴⁵ carried out two series of [3+2] cycloaddition reaction. Authors using commercially available trimethylsilyl azide (TMSN₃) as three atoms component and properly substituted (E)-2-phenyl-1-cyano-1-nitroethene and (Z)-2-aryl-1-carbomethoxy-1-nitroethenes as a CNAs. In a course of reaction catalysed by TBAF respective triazoles are created as a product of aromatization of primary formed triazoline systems.

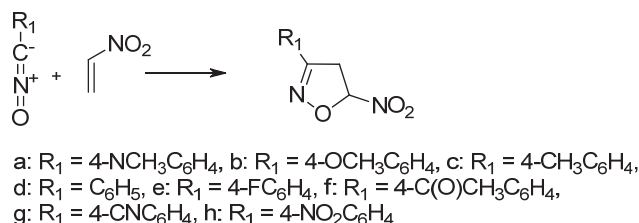
Another example application of azide in [3+2] cycloaddition reactions with CNAs, is the reaction between 1-bromo-3,3,3-trifluoro-1-nitropropene and phenyl azide (Scheme 10). In a course of reaction two of regioisomeric 1,2,3-triazoles are created, of which only 5-nitro-1-phenyl-4-(trifluoromethyl)-1*H*-1,2,3-triazole was isolated in pure form. The process is realized in temperature 20°C and diethyl ether as solvent. Conversion of substrates is about 14 days³⁴.

Table 14. Reaction of properly substituted 1-nitroethenes and trimethylsilyl azide

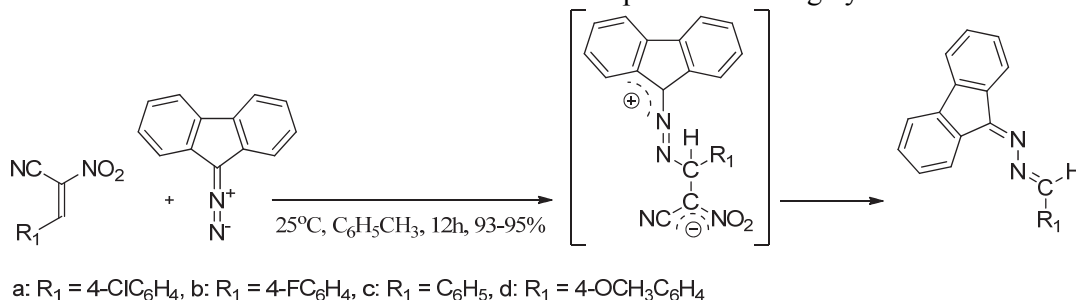
Entry	Nitroalkane	Temperature [°C]	Time [h]	Yield [%]
1	R ₁ =C ₆ H ₅ , R ₂ =CN	30	3	85
2	R ₁ =4-ClC ₆ H ₄ , R ₂ =CN	30	0.15	90
3	R ₁ =4-OCH ₃ C ₆ H ₄ , R ₂ =CN	30	3	75
4	R ₁ =4-OHC ₆ H ₄ , R ₂ =CN	30	3	70
5	R ₁ =5-(1,3-benzdioxole), R ₂ =CN	30	1	85
6	R ₁ =2-thiophene, R ₂ =CN	30	2	75
7	R ₁ =2-furan, R ₂ =CN	30	3	75
8	R ₁ =C ₆ H ₅ , R ₂ =CO ₂ CH ₂ CH ₃	50	7	80
9	R ₁ =4-ClC ₆ H ₄ , R ₂ =CO ₂ CH ₂ CH ₃	50	4	85
10	R ₁ =3-NO ₂ C ₆ H ₄ , R ₂ =CO ₂ CH ₂ CH ₃	50	7	85
11	R ₁ =4-CF ₃ C ₆ H ₄ , R ₂ =CO ₂ CH ₂ CH ₃	50	5	75
12	R ₁ =4-CNC ₆ H ₄ , R ₂ =CO ₂ CH ₂ CH ₃	50	6	70
13	R ₁ =4-OCH ₃ C ₆ H ₄ , R ₂ =CO ₂ CH ₂ CH ₃	80	8	70
14	R ₁ =2-OCH ₃ C ₆ H ₄ , R ₂ =CO ₂ CH ₂ CH ₃	80	8	75
15	R ₁ =3-OCH ₃ C ₆ H ₄ , R ₂ =CO ₂ CH ₂ CH ₃	80	9	70
16	R ₁ =2,4-(OCH ₃) ₂ C ₆ H ₄ , R ₂ =CO ₂ CH ₂ CH ₃	80	12	70

**Scheme 10.** [3+2] cycloaddition reactions 1-bromo-3,3,3-trifluoro-1-nitropropene and phenyl azide

The benzonitrile N-oxides have become the object of research in theoretical considerations. DFT calculations, for various levels in theory, show that [3+2] cycloaddition reactions between nitroethene and properly substituted analogs of benzonitrile N-oxides proceed by a one-step mechanism and should be considered polar, but not stepwise processes (Scheme 11). Moreover, a DFT calculations also showed that the favored reaction path leads to an adduct with a nitro group in position C5. It is compatible with experimental observations²⁸.

**Scheme 11.** [3+2] cycloaddition reactions between nitroethene and properly substituted analogs of benzonitrile N-oxides

Very interesting is example of reaction between diazafluorene and series of (E)-2-aryl-1-cyano-1-nitroethenes (Scheme 12). In the course of the reaction unexpectedly acyclic derivatives of 2,3-diazabuta-1,3-diene are formed instead of expected [3+2] cycloadducts containing pyrazoline skeleton. According to DFT calculations, the reaction course is a consequence of formation of zwitterionic structure in the first stage of the reaction and next, the cyanonitrocarbene elimination. Processes are realised in mild condition and are formed product with high yield³⁵.

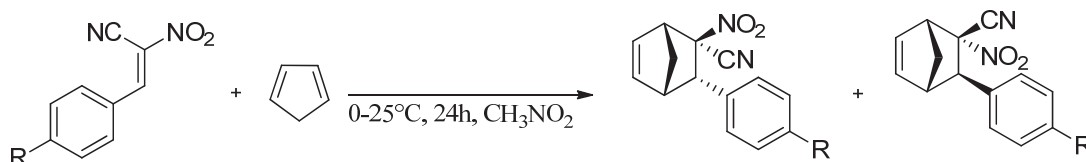


Scheme 12. Reaction between diazafluorene and series of (E)-2-aryl-1-cyano-1-nitroethenes.

2.3 Diels-Alder and Hetero Diels-Alder reactions

Jasiński et al.^{36,37}, explored a series of Diels-Alder reactions of 2-aryl-1-cyano-1-nitroethenes with cyclopentadiene in nitromethane which lead to *endo*- and *exo*-nitronorbornenes. After 24 hours, almost full conversion was achieved and the products (Table 15) were isolated by semipreparative HPLC. Authors also confirmed the structure of major product 5-cyano-5-nitro-6-phenyl-bicyclo[2.2.1]hept-2-ene by single crystal X-ray diffraction analysis³⁷.

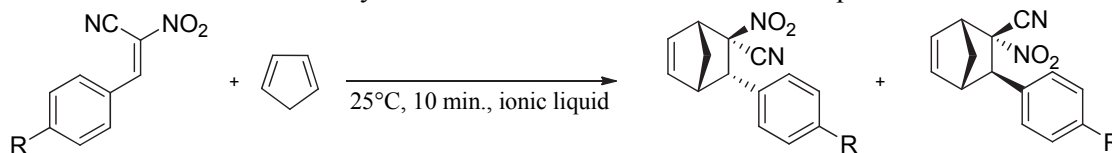
Table 15 Synthesis of *endo*- and *exo*- nitronorbornenes³⁶



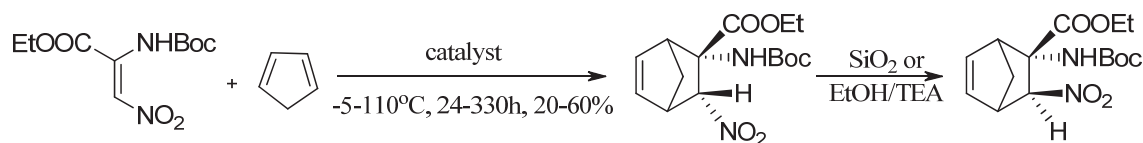
Entry	Nitroalkene	T [°C]	Products ratio
1	R=H	25	0.14
2	R=Cl	25	0.15
4	R=OCH ₃	25	0.08
3	R=Br	25	0.15
5	R=COOCH ₃	0	0.17
6	R=COOCH ₃	25	0.19

This team also presented a research on looking for better conditions for these processes and they performed cycloaddition of 2-aryl-1-cyano-1-nitroethenes to cyclopentadiene in ionic liquids³⁸. The authors proposed effective and eco-friendly method of obtained cycloadducts after only 10 minutes, and varying stereoselectivity which depended on the used ionic liquid (Table 16).

In turn, Caputo et al.³⁹, introduced the Diels-Alder reaction between ethyl (Z)-2-t-butoxycarbonylamino-3-nitroacrylate and cyclopentadiene in presence of different catalysts and conditions, which lead to ethyl (1R*,2S*,3R*,4S*)-2-t-butoxycarbonylamino-3-nitro-bicyclo[2.2.1]hept-5-ene-2-carboxylate with 20-60% yield (Table 17) which was not stable and was partially transformed into its epimer.

Table 16. Synthesis of nitronorbornenes in ionic liquids³⁸

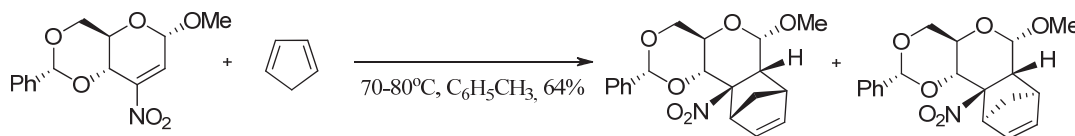
Entry	Nitroethene	Ionic liquid	Products ratio
1	R=H	[BMIM][Cl]	0.16
2	R=H	[TEAS][HSO ₄]	0.16
3	R=H	[HMIM][HSO ₄]	0.19
4	R=H	[C ₆ MIM][Cl]	0.14
5	R=H	[TEAP][H ₂ PO ₄]	0.13
6	R=H	[BMIM][BF ₄]	0.11
7	R=Cl	[BMIM][Cl]	0.17
8	R=OCH ₃	[BMIM][Cl]	0.24
9	R=F	[BMIM][Cl]	0.14
10	R=COOCH ₃	[BMIM][Cl]	0.12
11	R=CH ₃	[BMIM][Cl]	0.13

Table 17. Diels-Alder reaction of ethyl (Z)-2-t-butoxycarbonylamino-3-nitroacrylate and cyclopentadiene in the presence of different catalysts³⁹

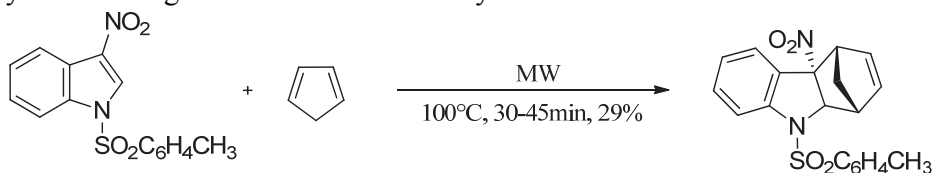
Entry	Catalyst	Solvent	T [°C]	Time [h]	Yield ^b [%]
1	EtAlCl ₂	CH ₂ Cl ₂	-5	24	-
2	Yb(OTf) ₄ ·H ₂ O	CH ₂ Cl ₂	25	24	-
3	Mg(ClO ₄) ₂	CH ₃ Cl	61	24	-
4	Mg(ClO ₄) ₂	C ₆ H ₅ CH ₃	110	24	-
5	Mg(ClO ₄) ₂	CH ₂ Cl ₂	25-40	24	30
6	Mg(ClO ₄) ₂	CH ₂ Cl ₂ ^a	25	12	-
7	EtAlCl ₂	Neat	-	330	20 ^c
8	Mg(ClO ₄) ₂	Neat	-	96	30 ^c
9	Mg(ClO ₄) ₂	Neat	-	330	40 ^c
10	-	Neat ^a	25	48	48 ^c
11	-	Neat ^a	25	48	60 ^d

^aultrasounds; ^bisolated compound; ^cproducts ratio=1:4; ^dproducts ratio=1:5

In 2011 *Mangione*⁴⁰ presented experimental and theoretical study of a Diels-Alder reaction between methyl 4,6-O-benzylidene-2,3-dideoxy-3-C-nitro- α -D-erythro-hex-2-enopyranoside and cyclopentadiene (Scheme 13). Treatment of nitroalkene with cyclopentadiene afforded to products in a 1.5:1 ratio and 64% yield. Quantum-chemical calculations also reproduced the experimentally observed endo/exoselectivities.

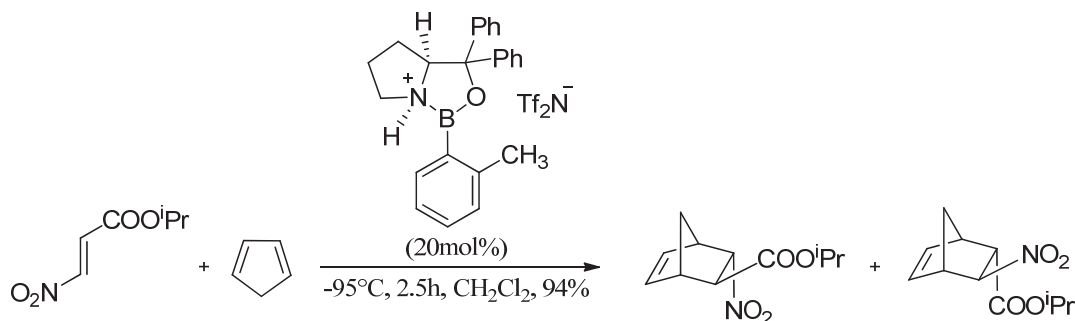
**Scheme 13.** Diels-Alder reaction between methyl 4,6-O-benzylidene-2,3-dideoxy-3-C-nitro- α -D-erythro-hex-2-enopyranoside and cyclopentadiene

Moreno's group⁴¹ also deal with reaction between 3-nitro-1-(p-toluenesulfonyl)indole with cyclopentadiene procced under microwave irradiation and solvent free conditions (Scheme 14). Diels-Alder cycloaddition gave carbazole with 29% yield.



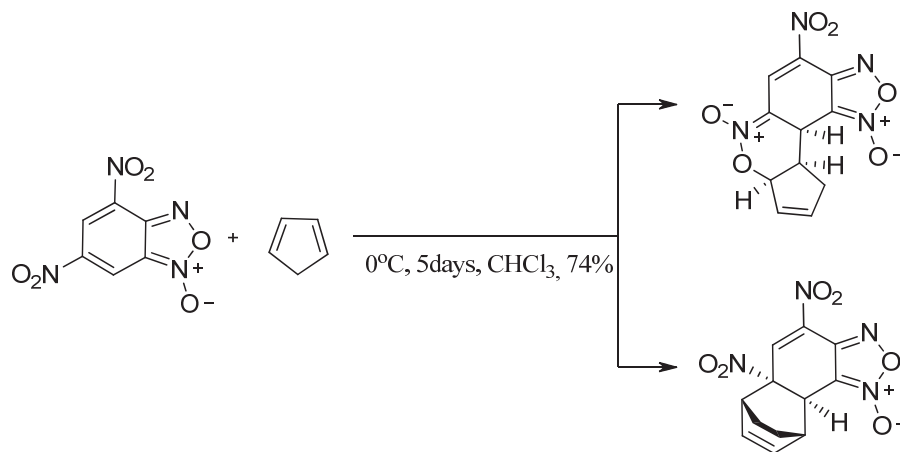
Scheme 14. Reaction between 3-nitro-1-(p-toluenesulfonyl)indole with cyclopentadiene

Mukherjee and *Corey*⁴² have studied the reaction of isopropyl β -nitroacrylate with cyclopentadiene and in the presence of proton-activated chiral oxazaborolidine cations (Scheme 15). The Diels-Alder reaction leads to mixture of adducts with 94% and in a ratio of 1.5:1, respectively.



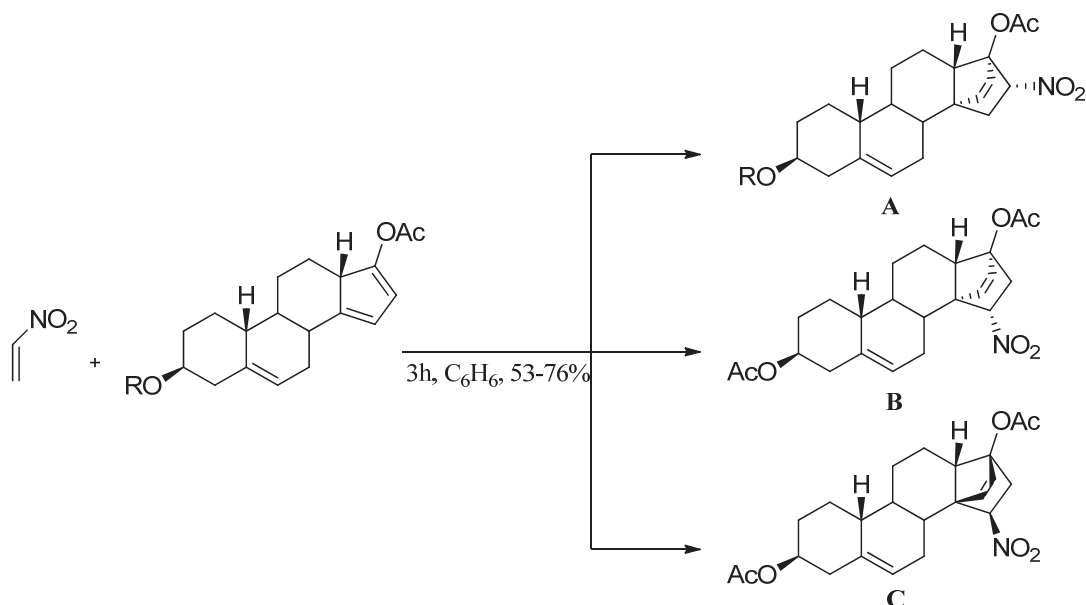
Scheme 15. Reaction of isopropyl β -nitroacrylate with cyclopentadiene.

In the case of reaction 4,6-dinitrobenzofuroxan with cyclopentadiene we are dealing with competition of Diels-Alder and Hetero Diels-Alder cycloadditions investigated by *Terrier's* group⁴³. The process proceeds stereoselectivity at 0°C and in chloroform to afford a products with 74% yield (Scheme 16).



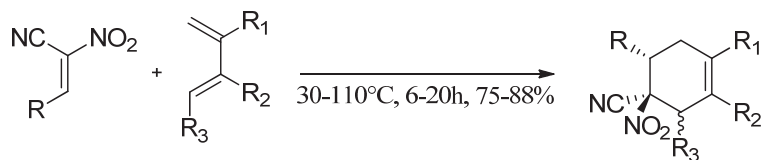
Scheme 16. Reaction 4,6-dinitrobenzofuroxan with cyclopentadiene

In turn, *Baranovsky* et al.⁴⁴, presented a Diels-Alder reaction of nitroethylene with androsa-14,16-dien-17-yl acetates. This cycloaddition leads to three adducts with yield 53-76% (Table 18) of which A is predominant (about 85% of the mixture) which in consequence can starting point for the synthesis natural steroids.

Table 18. Diels-Alder reactions of nitroethylene with androsa-14,16-dien-17-yl acetates⁴⁴

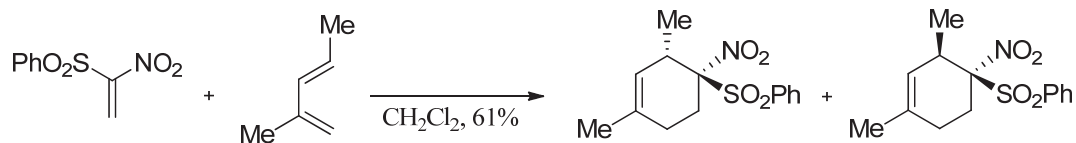
Entry	R	Yield [%]
1	Ac	76
2	Bz	53

A series of Diels-Alder cycloadditions nitroalkenes with four different 1,3-butadienes presented the *Pizzo* group⁵⁶. They conducted the reactions in solvent free conditions and generated *in situ* obtaining very good yields (75-88%) of cycloadducts (Table 19).

Table 19. Synthesis of cycloadducts in solvent-free conditions⁵⁶

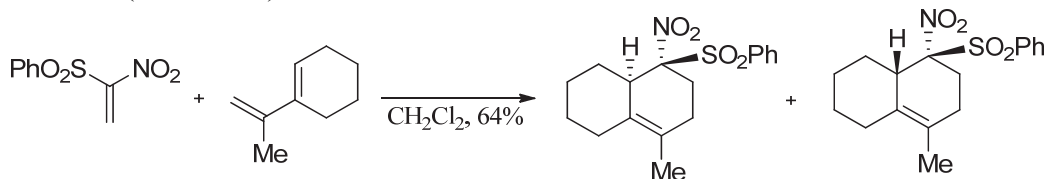
Entry	Nitroalkene	Diene	T [°C]	Time [h]	Yield [%]
1	C ₆ H ₅	R ₁ =R ₂ =CH ₃ , R ₃ =H	60	5	86
2	C ₆ H ₅	R ₁ =R ₂ =H, R ₃ =CH ₃	60	10	85
3	C ₆ H ₅	R ₁ =CH ₃ , R ₂ =R ₃ =H	60	12	80
4	(2,4-CH ₃ O)C ₆ H ₃	R ₁ =CH ₃ , R ₂ =R ₃ =H	30	12	80
5	(2,4,6-CH ₃ O)C ₆ H ₂	R ₁ =CH ₃ , R ₂ =R ₃ =H	30	12	78
6	(2,4-Cl)C ₆ H ₃	R ₁ =CH ₃ , R ₂ =R ₃ =H	60	6	84
7	(2-CH ₃)C ₆ H ₄	R ₁ =CH ₃ , R ₂ =R ₃ =H	60	6	85
8	(2-CH ₃ O)C ₆ H ₄	R ₁ =CH ₃ , R ₂ =R ₃ =H	60	20	88
9	(2-CF ₃)C ₆ H ₄	R ₁ =CH ₃ , R ₂ =R ₃ =H	30	12	77
10	(2-NO ₂)C ₆ H ₄	R ₁ =CH ₃ , R ₂ =R ₃ =H	30	12	78
11	(4-CN)C ₆ H ₄	R ₁ =CH ₃ , R ₂ =R ₃ =H	30	10	85
12	(2-Cl-6-F)C ₆ H ₃	R ₁ =CH ₃ , R ₂ =R ₃ =H	60	12	82
13	(3,5-Br-4-OH)C ₆ H ₂	R ₁ =CH ₃ , R ₂ =R ₃ =H	30	15	75
14	(4-CH ₃)C ₆ H ₄	R ₁ =R ₂ =R ₃ =H	110	12	75

Wade et al.⁴⁶, presented a reaction of (1-nitroethenyl) sulfonylbenzene with (*E*)-2-methyl-1,3-pentadiene (Scheme 17). This reaction gave diastereomeric (2,3-dimethyl-1-nitro-3-cyclohexene-1-yl)sulfonylbenzenes with 61% yield as an 80:20 isomeric mixture.



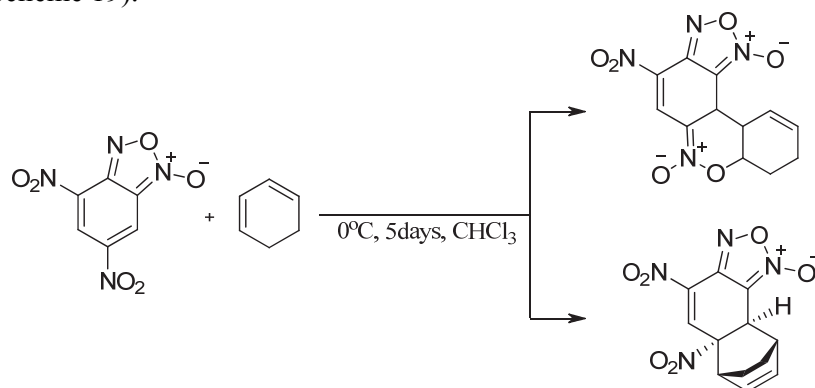
Scheme 17. Reaction of (1-nitroethenyl) sulfonylbenzene with (E)-2-methyl-1,3-pentadien.

The same group⁴⁶, deal with the Diels-Alder reaction with (1-nitroethenyl) sulfonylbenzene and 1-(1-methylethenyl)cyclohexene which gave diastereomeric cycloadducts in 64% yield as an 85:15 isomeric mixture (Scheme 18).

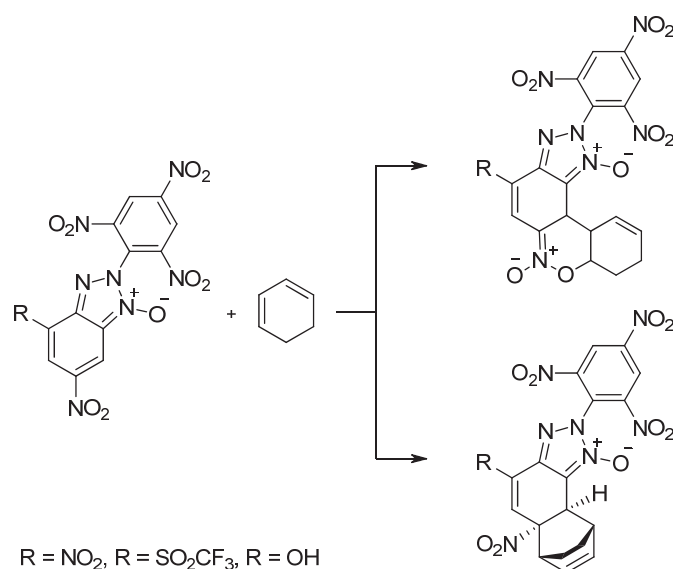


Scheme 18. Diels-Alder reaction with (1-nitroethenyl) sulfonylbenzene and 1-(1-methylethenyl)cyclohexene

Hallè et al.⁴⁷, presented an experimental study of the competition between Diels-Alder and Hetero Diels-Alder reactions. They explored of the addition of dinitrobenzofuroxane (DNBF) to cyclohexadiene affords a mixture of two diastereomeric Hetero Diels-Alder and Diels-Alder adducts in a 4:1 ratio (Scheme 19).



Scheme 19. Reaction of dinitrobenzofuroxane (DNBF) with cyclohexadiene

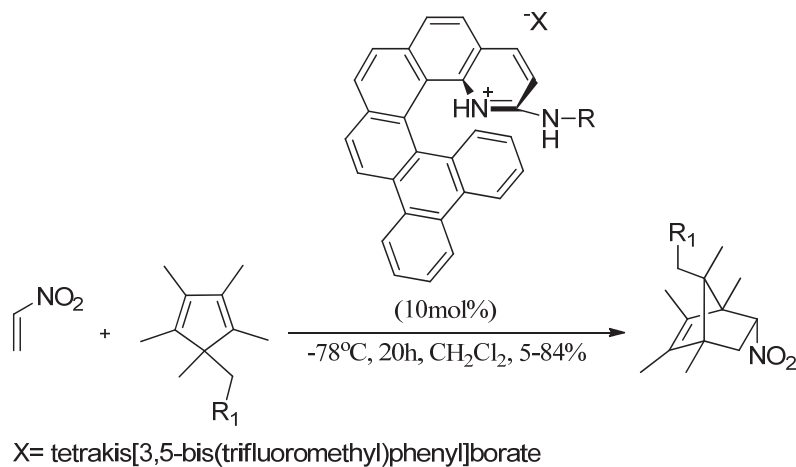


Scheme 20. Reaction between derivatives of 2-aryl-4,6-dinitrobenzotriazole-1-oxides and cyclohexadiene.

Ayadi and et al.⁴⁸, based on *Hallèworks*⁴⁷, conducted a theoretical study of reaction between derivatives of 2-aryl-4,6-dinitrobenzotriazole-1-oxides and cyclohexadiene. Theoretical studies shows that the only the reaction between 2-(2',4',6'-trinitrophenyl)-4,6-dinitrobenzotriazole-1-oxide is thermodynamically possible. Also in this case, we observed a competitive Diels-Alder reaction to Hetero Diels-Alder reaction (Scheme 20).

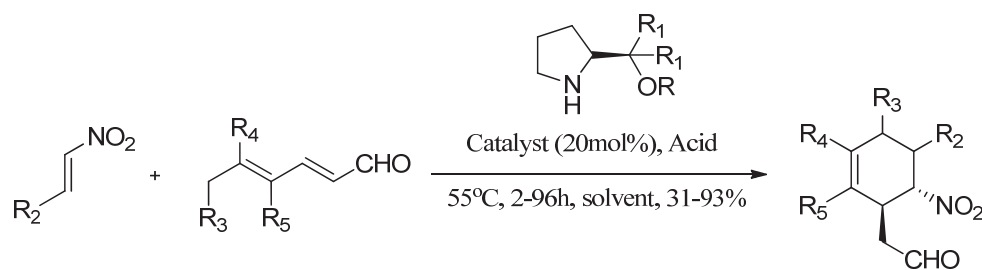
In 2012, *Narcis* et al.⁴⁹, submitted the periselective Diels-Alder reaction of nitroethylene with 5-substituted pentamethylcyclopentadienes which has been realized by helical-chiral hydrogen bond donor catalysts – (M)-catalysts. Cycloadducts are obtained in this reactions with relatively high yields 38-84% (Table 20).

Table 20. Diels-Alder reactions of nitroalkenes with dienes and in presence of different catalysts⁴⁹



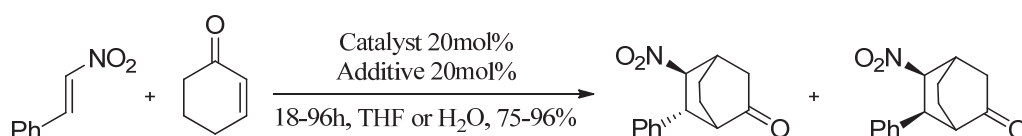
Entry	Catalyst, R	Dienes	Yields [%]
1	-	R ₁ =C ₆ H ₅	<5
2		R ₁ =C ₆ H ₅	70
3		R ₁ =C ₆ H ₅	84
4		R ₁ =C ₆ H ₅	70
5		R ₁ =C ₆ H ₅	70
6		R ₁ =C ₆ H ₅	77
7		R ₁ =4-FC ₆ H ₄	80
8		R ₁ =4-ClC ₆ H ₄	38
9		R ₁ =3-ClC ₆ H ₄	67

Chen et al.⁵⁰, presented the first asymmetric Diels-Alder reaction of nitroalkenes and 2,4-dienals by a newly developed trienamine catalysis. Many diversely substituted 2,4-dienals and nitroalkenes have been explored, generally giving densely substituted chiral cyclohexene derivatives in high diastereo- and enantioselectivities (Table 21).

Table 21. Diels-Alder reactions of nitroalkenes with dienes and in presence of trienamine catalysts⁵⁰

Entry	Catalyst	Nitroalkenes	Dienes	Solvent	Time [h]	Yields [%]
1	R=TMS, R ₁ =Ph	R ₂ = C ₆ H ₅	R ₃ =R ₄ =R ₅ =H	CHCl ₃	72	59
2	R=TMS, R ₁ =Ph	R ₂ = C ₆ H ₅	R ₃ =R ₄ =R ₅ =H	CHCl ₃	2	87
3	R=TMS, R ₁ =Ph	R ₂ = C ₆ H ₅	R ₃ =R ₄ =R ₅ =H	MeCN	96	43
4	R=TMS, R ₁ =Ph	R ₂ = C ₆ H ₅	R ₃ =R ₄ =R ₅ =H	MeC ₆ H ₅	96	55
5	R=TMS, R ₁ =Ph	R ₂ = C ₆ H ₅	R ₃ =R ₄ =R ₅ =H	C ₄ H ₈ O	96	75
6	R=TMS, R ₁ =Ph	R ₂ = C ₆ H ₅	R ₃ =R ₄ =R ₅ =H	CHCl ₃	6	79
7	R=TMS, R ₁ =Ph	R ₂ = C ₆ H ₅	R ₃ =R ₄ =R ₅ =H	CHCl ₃	6	71
8	R=TES, R ₁ =Ph	R ₂ = C ₆ H ₅	R ₃ =R ₄ =R ₅ =H	CHCl ₃	3	87
9	R=TMS, R ₁ =4-MeO-3,5-tBu ₂ C ₆ H ₂	R ₂ = C ₆ H ₅	R ₃ =R ₄ =R ₅ =H	CHCl ₃	3	75
10	R=TMS, R ₁ =3,5-(CF ₃) ₂ C ₆ H ₃	R ₂ = C ₆ H ₅	R ₃ =R ₄ =R ₅ =H	CHCl ₃	96	31
11	R=TMS, R ₁ = C ₆ H ₅	R ₂ = C ₆ H ₅	R ₃ =R ₄ =R ₅ =H	CHCl ₃	17	85
12	R=TMS, R ₁ = C ₆ H ₅	R ₂ =2-BrC ₆ H ₄	R ₃ =R ₄ =R ₅ =H	CHCl ₃	2	85
13	R=TMS, R ₁ = C ₆ H ₅	R ₂ =3-ClC ₆ H ₄	R ₃ =R ₄ =R ₅ =H	CHCl ₃	3	82
14	R=TMS, R ₁ = C ₆ H ₅	R ₂ =4-BrC ₆ H ₄	R ₃ =R ₄ =R ₅ =H	CHCl ₃	2	87
15	R=TMS, R ₁ = C ₆ H ₅	R ₂ =3,4-Cl ₂ C ₆ H ₃	R ₃ =R ₄ =R ₅ =H	CHCl ₃	2	89
16	R=TMS, R ₁ = C ₆ H ₅	R ₂ =3-MeC ₆ H ₄	R ₃ =R ₄ =R ₅ =H	CHCl ₃	5	84
17	R=TMS, R ₁ = C ₆ H ₅	R ₂ =3-MeC ₆ H ₄	R ₃ =R ₄ =R ₅ =H	CHCl ₃	5	89
18	R=TMS, R ₁ = C ₆ H ₅	R ₂ =2-thienyl	R ₃ =R ₄ =R ₅ =H	CHCl ₃	2	87
19	R=TMS, R ₁ = C ₆ H ₅	R ₂ =4-furyl	R ₃ =R ₄ =R ₅ =H	CHCl ₃	24	73
20	R=TMS, R ₁ = C ₆ H ₅	R ₂ = C ₆ H ₅	R ₃ =R ₅ =CH ₃ , R ₄ =H	CHCl ₃	7	89
21	R=TMS, R ₁ = C ₆ H ₅	R ₂ =2-thienyl	R ₃ =R ₄ =H, R ₅ = C ₆ H ₅	CHCl ₃	3	90
22	R=TMS, R ₁ = C ₆ H ₅	R ₂ = C ₆ H ₅	R ₃ =CH ₃ , R ₄ =H, R ₅ =C ₆ H ₅	CHCl ₃	2	93

Xu et al.⁵¹, presented a series of Diels-Alder reactions of 1-nitro-2-phenylethene with cyclohexenones provide in the presence of organocatalysts. Authors conducted these reactions in various conditions and in attendance of different organocatalysts. Products are obtained with high yield 75-96% (Table 22).

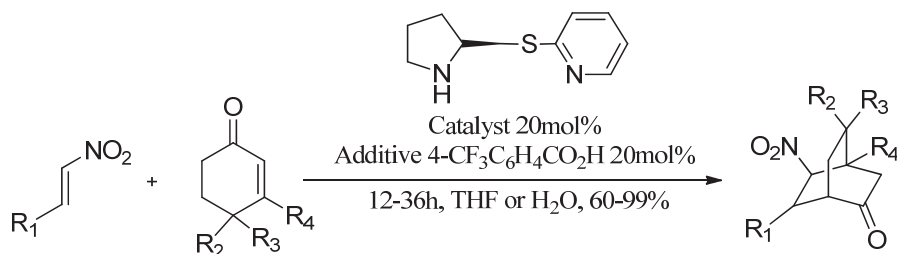
Table 22. Reaction of nitroalkene with cyclohexenones and different organocatalysts⁵¹

Entry	Catalyst	Additive	Time [h]	Yield [%]
1		C ₆ H ₅ CO ₂ H	96	80
2		C ₆ H ₅ CO ₂ H	24	82

3		$C_6H_5CO_2H$	24	75
4		$C_6H_5CO_2H$	24	85
5		$C_6H_5CO_2H$	20	82
6		$C_6H_5CO_2H$	20	85
7		CH_3CO_2H	18	82
8		CF_3CO_2H	24	84
9		2-C10H7SO3	24	84
10		4-NO ₂ C ₆ H ₄ CO ₂ H	20	90
11		3-NO ₂ C ₆ H ₄ CO ₂ H	20	85
12		2-NO ₂ C ₆ H ₄ CO ₂ H	24	88
13		4-CF ₃ C ₆ H ₄ CO ₂ H	20	95
14		2-CF ₃ C ₆ H ₄ CO ₂ H	24	89
15		4-FC ₆ H ₄ CO ₂ H	24	93
16		4-CF ₃ C ₆ H ₄ CO ₂ H	20	94
17		4-CF ₃ C ₆ H ₄ CO ₂ H	20	96

Authors, among all used catalyst, chose the most suitable one for Diels-Alder reaction in terms of conversion and enantioselectivity. Authors⁵¹, also carried out a series of reactions nitroalkenes and cyclohexenones in the presence of catalyst which lead to products with 60-99% yields (Table 23).

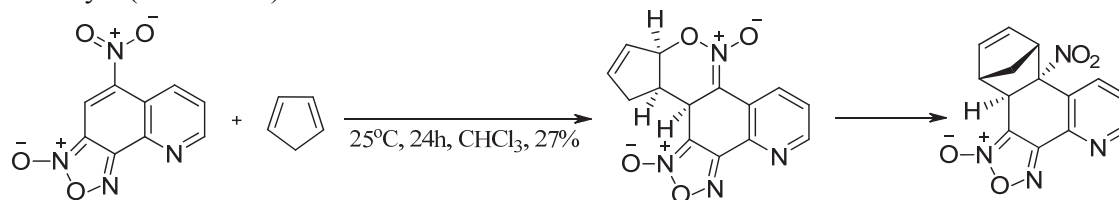
Table 23. Diels-Alder reactions of nitroalkenes with cyclohexenones in the presence of organocatalyst⁵¹



Entry	Nitroalkene	Cyclohexenones	Time [h]	Yield [%]
1	R ₁ =2-MeOC ₆ H ₄	R ₂ =R ₃ =R ₄ =H	20	60
2	R ₁ =3-MeOC ₆ H ₄	R ₂ =R ₃ =R ₄ =H	12	80
3	R ₁ =4-MeOC ₆ H ₄	R ₂ =R ₃ =R ₄ =H	20	98
4	R ₁ =3-MeC ₆ H ₄	R ₂ =R ₃ =R ₄ =H	20	97
5	R ₁ =Ph	R ₂ =R ₃ =R ₄ =H	20	98
6	R ₁ =4-FC ₆ H ₄	R ₂ =R ₃ =R ₄ =H	20	97
7	R ₁ =4-ClC ₆ H ₄	R ₂ =R ₃ =R ₄ =H	20	99
8	R ₁ =3-BrC ₆ H ₄	R ₂ =R ₃ =R ₄ =H	12	55
9	R ₁ =4-BrC ₆ H ₄	R ₂ =R ₃ =R ₄ =H	12	92
10	R ₁ =3-NO ₂ C ₆ H ₄	R ₂ =R ₃ =R ₄ =H	12	70
11	R ₁ =4-CF ₃ C ₆ H ₄	R ₂ =R ₃ =R ₄ =H	12	98
13	R ₁ =Ph	R ₂ =R ₃ =H, R ₄ =Me	36	95
14	R ₁ =Ph	R ₂ =R ₃ =Me, R ₄ =H	20	96

Recently published experimental and quantum-chemical studies⁵², confirm that the reaction between nitrofuoroquinoline and cyclopentadiene lead to Hetero Diels-Alder cycloadduct which next convert spontaneously according to the mechanism of [3,3] sigmatropic rearrangement into more thermodynamically stable, experimentally detected Diels-Alder cycloadduct. Both Hetero Diels-Alder

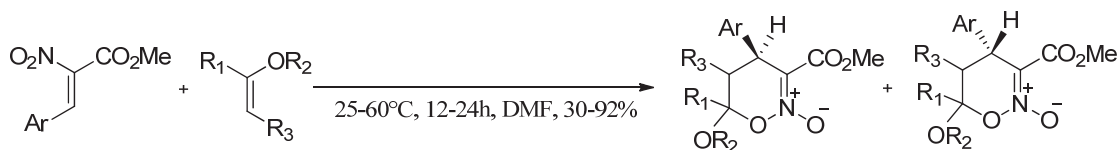
and Diels-Alder cycloadducts have been experimentally isolated and obtained with 27% and 60% yield, respectively⁵² (Scheme 21).



Scheme 21. Reaction between nitrofuoroquinoline and cyclopentadiene.

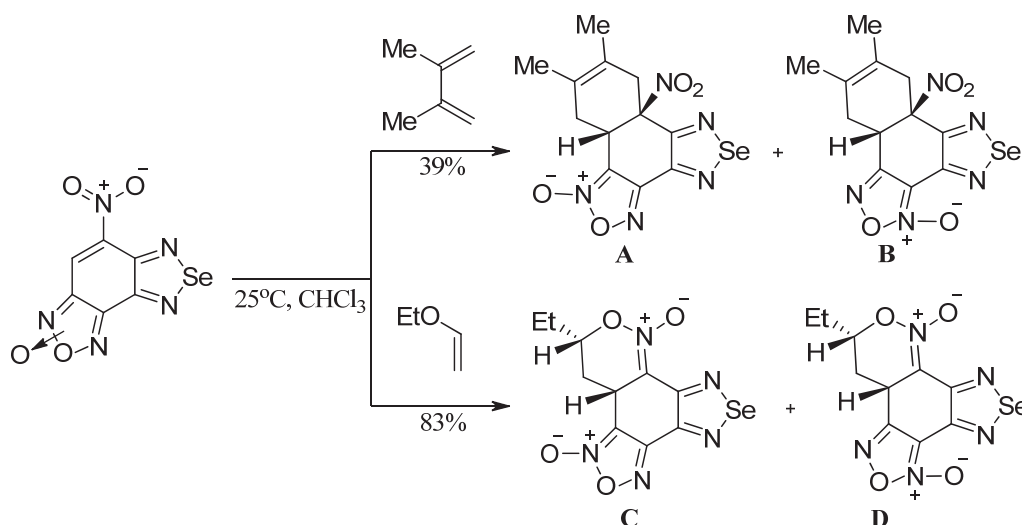
In 1988, *Tohda et al.*⁵³, presented a Hetero Diels-Alder cycloaddition of (*Z*)-methyl α,β -dinitrocinnamate with vinyl ethers. These reactions lead to 6-alkoxy-5,6-dihydro-4H-1,2-oxazine 2-oxides with yield 30-92% (Table 24).

Table 24. Reaction of methyl α,β -dinitrocinnamate with vinyl ethers⁵³



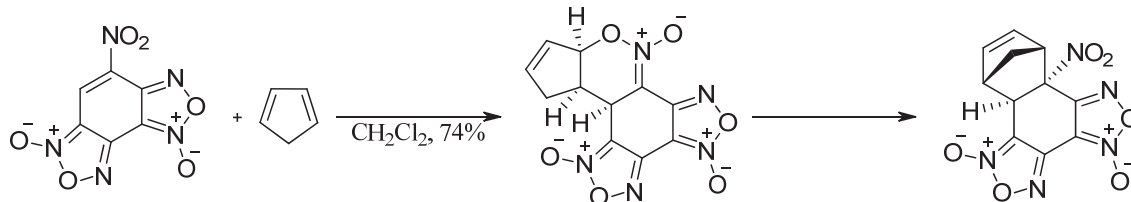
Entry	Vinylether	T [°C]	Time [h]	Yield [%]
1	R ₁ =R ₃ =H, R ₂ =C ₂ H ₅	25	24	92
2	R ₁ =H, R ₂ =R ₃ =(CH ₂) ₂ -	60	12	90
3	R ₁ =H, R ₂ =R ₃ =(CH ₂) ₃ -	60	12	30
4	R ₂ =CH ₃ , R ₁ =R ₃ =(CH ₂) ₃ -	50	12	84
5	R ₁ =CH ₃ , R ₂ =R ₃ =(CH ₂) ₄ -	50	12	72

*Бастраков et al.*⁵⁴, in Diels-Alder reactions between 1-oxide-5-nitro [1,2,5]selenodiazole[3,4-*e*][2,1,3]-benzoxadiazole and 2,3-dimethyl-1,3-butadiene or ethyl vinyl ether synthesized the cycloadducts representing complex hybrid molecules with biological important fragments. Products are obtained with 39% (**A**, **B**) and 83% (**C**, **D**) yields (Scheme 22).



Scheme 22. Diels-Alder reactions between 1-oxide-5-nitro [1,2,5]selenodiazole[3,4-*e*][2,1,3]-benzoxadiazole and 2,3-dimethyl-1,3-butadiene

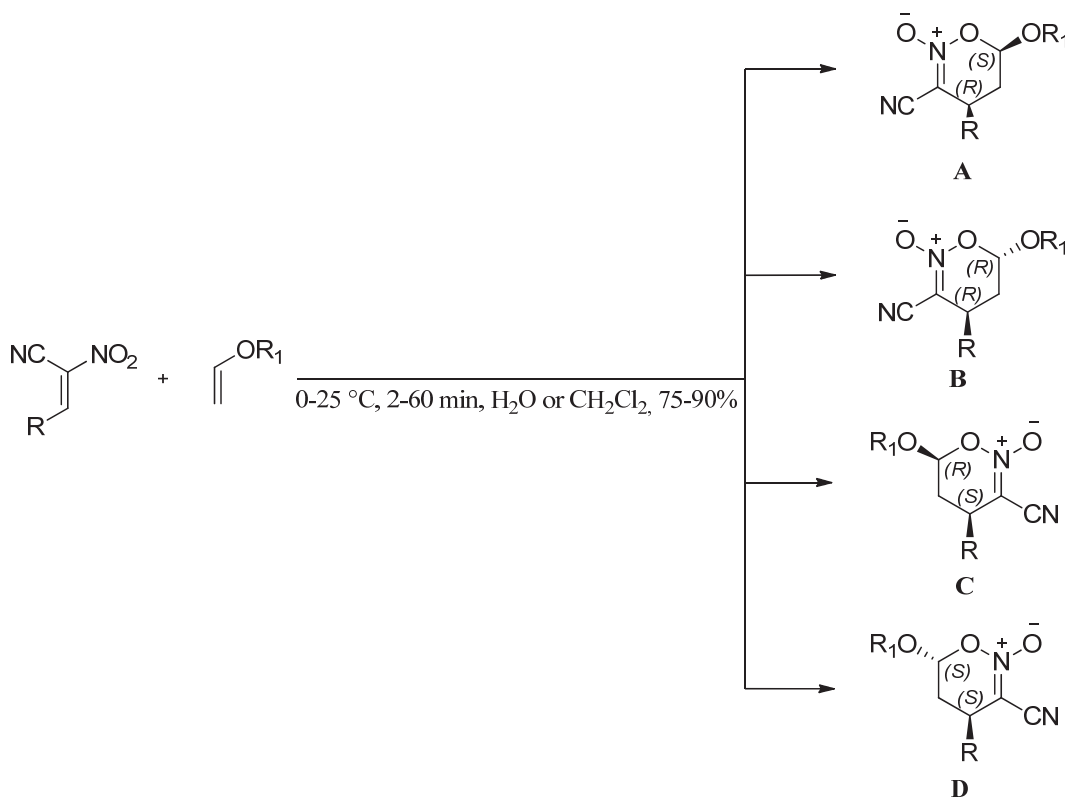
Goumont group⁵⁵, combining the information provided by DFT calculations and experimental studies, examined the mechanism of 4-nitrobenzodifuroxan with cyclopentadiene (Scheme 23). At the beginning of this reaction, proceed the formation of Hetero Diels-Alder adduct with 74% yield and then being followed by its conversion into Diels-Alder cycloadduct via a [3+3] sigmatropic shift.



Scheme 23. Reaction of 4-nitrobenzodifuroxan with cyclopentadiene.

Fringuelli et al.⁵⁶ in 2001, represented the study about Hetero Diels-Alder cycloaddition (E)-2-aryl-1-cyano-1-nitroalkenes with chiral and enantiopure vinyl ethers. These reactions lead to mixture of diastereoisomer of nitronates (**A-D**) with very high yield (75-90%) (Table 25). Kinetics aspects of these transformations presented the *Jasiński* group⁵⁷.

Table 25. Hetero Diels-Alder Cycloadditions of nitroalkenes with vinyl ethers⁵⁶

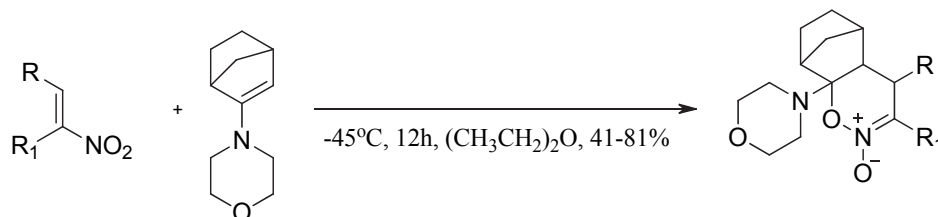


Entry	Nitroalkenes	Vinyl ethers	T [°C]	Time [min]	Products [%]				Yield [%]
					A	B	C	D	
1	R=C ₆ H ₅		0	3	80	20	-	-	75
2	R=(4-Cl)C ₆ H ₄	R ₁ =C ₂ H ₅	0	20	96	4	-	-	90
3	R=(4-OMe)C ₆ H ₄		25	10	98	2	-	-	85
4	R=(4-Cl)C ₆ H ₄		0	30	35	6	54	5	-

5	R=(4-Cl)C ₆ H ₄		0	30	30	5	60	5	-
6	R=C ₆ H ₅		25	60	-	-	85	15	-
7	R=(4-Cl)C ₆ H ₄		0	60	-	-	85	15	-
8	R=(4-OMe)C ₆ H ₄		25	60	-	-	83	17	-

In 2001, *Valentin et al.*⁵⁸, concerned with the Hetero Diels-Alder cycloaddition reactions of cyclic and acyclic conjugated nitroalkenes with morpholino enamine of 2-norbornanone. Formation of corresponding 1,2-oxazine N-oxides succeed with 41-81% yield (Table 26).

Table 26. Hetero Diels-Alder Cycloadditions nitroalkenes with morpholino enamine of 2-norbornanone⁵⁸



Entry	Nitroalkene	Yield [%]
1	R=R ₁ =H	-
2	R=H, R ₁ =CH ₃	72
3	R=H, R ₁ =C ₆ H ₅	41
4	R=CH ₃ , R ₁ =H	63
5	R=CH ₃ , R ₁ =CH ₃	63
6	R=CH ₃ , R ₁ =C ₆ H ₅ ; CH ₃	62
7	R=C ₆ H ₅ , R ₁ =H	65
8	R=C ₆ H ₅ , R ₁ =CH ₃	81
9	R=R ₁ =C ₆ H ₅	44
10	R=R ₁ =-(CH ₂) ₃ -	61
11	R=R ₁ =-(CH ₂) ₄ -	68

3. Conclusions

Recent years brought a series of significant reports on the reactivity of conjugated nitroalkenes in the cycloadditions reactions. Moreover - due to the rapidly growing availability of high-powered computers - a thorough analysis of the mechanism of a number of these reactions has been made, often throwing new light on the way of converting substrates.

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