Translated from *Uspekhi Khimii*, **44**, 744-758 (1975) U.D.C. 547.311.2;547.317.2

Nitroacetylenes

K.B.Rall', A.I.Vil'davskaya, and A.A.Petrov

The review examines the methods of synthesis, structures, infrared, ^{1}H NMR, and ultraviolet spectra, and physical and chemical properties of a new class of compounds—nitroacetylenes.
The bibliography includes 83 references.

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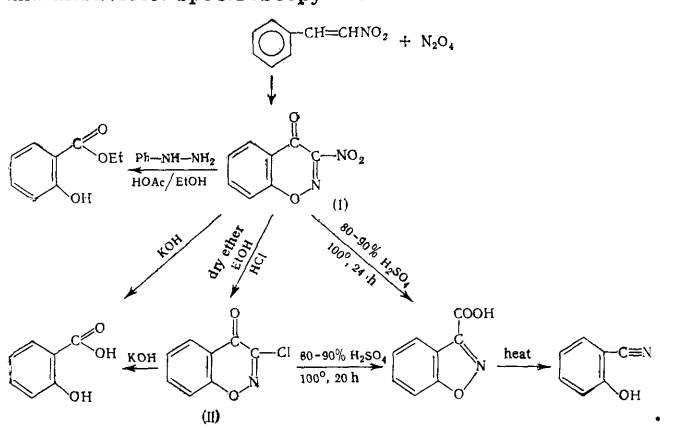
I. INTRODUCTION

Nitroacetylenes constitute a new, still little investigated class of organic compounds which is interesting in view of a combination of the energy-deficient triple bond and the electron-accepting nitro-group. α-Acetylenic nitro-compounds, where the conjugation of the π-electron system with the electrophilic nitro-group leads to extensive possibilities of their employment in organic synthesis, have attracted particular attention.

Whereas extensive data were available as early as 1950 on the methods of synthesis and a wide variety of reactions of ethylenic nitro-compounds, systematic study of acetylenic nitro-compounds did not begin essentially until 1969. This paper surveys the results of studies published until the beginning of 1973.

The first mention of nitroacetylenes dates back to 1903[1] when Wieland obtained by the reaction of nitrogen oxides with cinnamaldehyde a low yield of a yellow crystalline substance having the overall formula $C_8H_4N_2O_4$. On the basis of elemental analysis and the determination of molecular weight, Wieland erroneously attributed to this compound the structure of *p*-nitrophenylnitroacetylene. However, the author did not rule out other possible structures.

p-Nitrophenylnitroacetylene was probably obtained for the first time much later by Novikov et al.[2] by nitrating β-nitrostyrene with nitrogen tetroxide, but attempts to reproduce this reaction were unsuccessful: instead of nitroacetylene, the product isolated was (probably the same as in Wieland's reaction[1]) 1-nitro-2-azachromone (3-nitro-4*H*-1,2-benzoxazin-4-one)[3] (I), whose structure has been demonstrated chemically and by ^{1}H NMR, infrared, and ultraviolet spectroscopy[3-5]:



Later heavy dark-red oils were obtained by the dehydrohalogenation with the aid of amines of 1-bromo-1-nitroalkenes[6] and 1-bromo-1-nitro-2-phenylethylene[7]; the structure of α-nitroacetylenes was attributed to the oils.

Thus, on treatment with diethylamine, 1-bromo-1-nitro-2-phenylethylene was converted into an oil which exploded on distillation, reacted instantly with Baeyer's reagent, and did not decolorise bromine water. The molecular weight and the nitrogen content corresponded to the formula of phenylnitroacetylene. However, these experiments could not be reproduced either[3].

It was not until 1969 that Jäger and Viehe described for the first time a reliable method for the synthesis of t-butylnitroacetylene and its homologues[8]. These investigations were subsequently extended[3].

Among non-conjugated nitroacetylenes, only the hexanitro-derivative has so far been obtained[9].

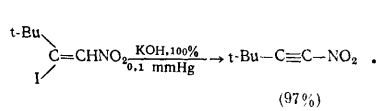
1,1,1,6,6,6-Hexanitrohex-3-yne[9], 1-nitroalk-1-ene-3-ynes[10-13], and a number of nitrobutenyne derivatives of the elements (silicon and germanium)[14] were also obtained recently. Among functional derivatives of nitroacetylenes, only glycols are known[15,16].

II. THE PREPARATION OF NITROACETYLENES

The simplest α-nitroacetylenes were obtained (by analogy with nitroalkenes) by the dehydrohalogenation of halogenonitroalkenes formed as a result of the addition of NO_2X (X = Cl[17-20] or X = I[21]) to acetylenic compounds.

Nitroiodination proved to be most suitable for this purpose. Difficulties arose in the second reaction stage (dehydroiodination), for which various reagents were employed[3]: tertiary amines, sodium acetate in dimethylformamide (DMF), silver oxide in ether, and potassium t-butoxide; the reaction was followed by the intensity of the band due to the triple bond in the infrared spectra of the final product. Potassium hydroxide proved to be the most effective dehydrohalogenating agent.

Thus, by passing 2-iodo-3,3-dimethyl-1-nitrobut-1-ene (III) through a tube with alkali heated to 110–120°C, t-butylnitroacetylene (IV) was obtained (yield 96–97%, purity of the product according to gas–liquid chromatographic data 98–100%):



Nitroacetylenes with isopropyl (V, yield 74%) and n-propyl (VI, yield 28%) groups were obtained similarly. n-Butyl-α-nitroacetylene was isolated from a mixture with the starting material. The formation of phenylnitroacetylene was demonstrated spectroscopically ($\nu C{\equiv}C$ = 2240 cm^{-1}); its low volatility made its further purification difficult[3].

Stereoisomeric mixtures of the initial iodonitroalkenes were usually dehydroiodinated. The use of pure *cis*- and *trans*-isomers did not increase the yield.

1,1,1,6,6,6-Hexanitrohex-3-yne (VII) was obtained in 72% yield by the double decomposition reaction between 1,4-dibromobut-2-yne and the silver salt of trinitromethane[9]:

$$BrCH_2{-}C{\equiv}C{-}CH_2Br + 2AgC(NO_2)_3 \rightarrow \underset{\text{(VII)}}{(NO_2)_3C{-}CH_2{-}C{\equiv}C{-}CH_2{-}C(NO_2)_3} + 2AgBr\ .$$

4-Trialkylsilyl(germyl)-1-nitrobut-1-ene-3-ynes are formed when products of the addition of nitrogen tetroxide and iodine to the corresponding vinylacetylene derivatives of the elements are dehydroiodinated by lead acetate[12-14]. The hydrolytic cleavage of the C–E bond (where E is an element) in butenyne derivatives of the elements leads to 1-nitrobut-1-en-3-yne[11] (VIII):

$$CH_2{=}CH{-}C{\equiv}C{-}Si\,(Ge)\,R_3 \xrightarrow{N_2O_4,I_2} NO_2CH_2{-}CHI{-}C{\equiv}C{-}Si\,(Ge)\,R_3 \rightarrow$$
$$\rightarrow NO_2CH{=}CH{-}C{\equiv}C{-}Si\,(Ge)\,R_3 \xrightarrow{8M\ HClO_4} \underset{\text{(VIII)}}{NO_2CH{=}CH{-}C{\equiv}CH}\ .$$

Acetylenic nitroglycols have been obtained by the condensation of acetylenic aldehydes with nitroalcohols[15,16]:

$$R{-}C{\equiv}C{-}\overset{\overset{O}{\parallel}}{C}{-}H + NO_2CH_2{-}CH_2OH \rightarrow R{-}C{\equiv}C{-}CH(OH){-}CHNO_2{-}CH_2OH\ .$$

III. STRUCTURE AND PHYSICAL PROPERTIES

The study of the physical properties of α-nitroacetylenes led to definite conclusions concerning the conjugation of the highly electrophilic nitro-group with the C≡C bond.

α-Nitroacetylenes are pale yellowish-green liquids with a strong lachrymatory smell resembling that of lower nitro-olefins.

Table 1. Ultraviolet spectra of α-nitroalkylacetylenes and their ethylenic analogues[3].

No.	Compound	$\lambda_1(\pi{-}\pi^*)$ nm	lg ε_1	$\lambda_2(\pi{-}\pi^*)$ nm	lg ε_2	Solvent
1	t-Bu–C≡CNO_2	238	3.90	290	1.5	n-Hexane
2	i-Pr–C≡CNO_2	239	3.84	290	2.2	Cyclohexane
3	n-Pr–C≡CNO_2	235	3.88	290	2.7	n-Hexane
4	t-Bu–CH=$CHNO_2$ (*trans*)	228	4.02	310–320	2.8	n-Heptane
5	i-Pr–CH=$CHNO_2$ (*trans*)	227	3.70	—	—	n-Heptane
6	Me–CH=$CHNO_2$ (*trans*)	225	4.01	295–310	2.9	n-Heptane

The ultraviolet spectra of nitroacetylenes resemble those of *trans*-nitro-olefins. The short-wavelength ultraviolet band of nitroacetylenes undergoes a bathochromic shift relative to nitro-olefins and the extinction coefficient is reduced, which is characteristic of acetylenic systems in relation to their ethylenic analogues[22].

It has been suggested that the absorption at 290 nm (shoulder) is associated with a weak $\pi{-}\pi^*$ transition in the nitro-group of the $C{\equiv}CNO_2$ fragment[22,23].

The asymmetric stretching vibration band of the conjugated nitro-group in the spectra of α-ethylenic nitro-compounds is in the range 1517–1530 cm^{-1} and the band due to the symmetrical stretching vibrations is in the range ~ 1340–1350 cm^{-1}. The difference between the asymmetric and symmetric stretching vibration wavenumbers, which is an important characteristic of nitro-olefins, thus amounts to $\Delta\nu \simeq 180$ cm^{-1}. The substitution of a hydrogen atom at the β-carbon atom in nitroalkenes by a bromine atom leads to an increase of the asymmetric vibration wavenumber, a decrease of the symmetric vibration wavenumber, and an appreciable increase of the difference between them ($\Delta\nu = 218 \pm 7$ cm^{-1})[24,25].

Table 2. Characteristic wavenumbers in the infrared spectra of nitroacetylenes[3].

Compound	ν_{NO_2}, cm^{-1}		$\nu_{C\equiv C}$, cm^{-1}	ν_{C-N}, cm^{-1}
	asym.	sym.		
t-Bu–C≡CNO_2	1515	1330	2235 (s.) 2270 (w.)	730
i-Pr–C≡CNO_2	1510	1345	2245 (s.) 2210 (w.)	730
n-Pr–C≡CNO_2	1515	1348	2260 (s.) 2200 (w.)	730

Table 3.

Compound	$\nu_{C\equiv C}$, cm^{-1}		References
t-Bu–C≡CH	2105		28
t-Bu–C≡C–$CONH_2$	2245	2230	3
t-Bu–C≡C–COOEt	2260	2230	3
t-Bu–C≡C–CN	2325	2270	3
t-Bu–C≡C–NMe_2	2260	2230	3
t-Bu–C≡C–N(Ph)Me	2280	2245	3
t-Bu–C≡C–NO_2	2270	2235	3
t-Bu–C≡C–Cl	2243	2170	27
t-Bu–C≡C–Br	2216		27
t-Bu–C≡C–I	2191		27
$Me_3SiC{\equiv}C{-}NO_2$	2165		27
$Me_3SiC{\equiv}C{-}Cl$	2137		27
$Me_3SiC{\equiv}C{-}Br$	2126		27
$Me_3SiC{\equiv}C{-}I$	2100		27

The symmetric and asymmetric stretching vibration bands of the nitro-group in the infrared spectra of nitroacetylenes are very intense, the latter being displaced towards shorter wavelengths (1510–1515 cm^{-1}) compared with nitro-olefins and halogenonitro-olefins[3,24,25]; $\Delta\nu \simeq$ 165 cm^{-1}. The conjugation of the nitro-group with the multiple bond apparently has the greatest effect on the intensity of the symmetric stretching vibration band of the nitro-group: in the spectra of nitroacetylenes this band is much more intense than the band of the asymmetric vibrations, while in the spectra of nitro-olefins the intensities of these bands are approximately equal (in the spectra of aliphatic nitroalkanes the symmetrical stretching vibration bands of the nitro-group are of moderate intensity)[26].

The infrared spectra of α-nitroacetylenes show a splitting of the absorption band of the triple bond (Table 2), which is characteristic of disubstituted acetylenes (for

example, of trifluoropropyne and perfluorodimethylacetylene[3,27]; see also Table 3). The additional bands are accounted for by mechanical interactions; they are also regarded as overtones or combination bands. However, the reason for the splitting of the absorption band of the triple bond still remains controversial[22,27,28].

Comparison of the infrared spectra of halogenoacetylenes containing t-butyl and trimethylsilyl groups showed that in the latter case $\nu C\equiv C$ is reduced by 106–90 cm^{-1}.

In relation to t-butylnitroacetylene, the stretching vibration band of the C≡C bond in trimethylsilylnitroacetylene ($\nu C\equiv C$ = 2165 cm^{-1}) undergoes a steady bathochromic shift by about 10 cm^{-1} and its intensity falls, which may be a consequence of the $\pi-d$ interaction in the $\rangle Si-C\equiv C$ group.

The 730 cm^{-1} band, which can be assigned to the C–N stretching vibrations, is constant in the spectra of all nitroacetylenes[3]. The information about the ^1H NMR spectra of nitroalkenes is extremely limited[29,30].

The ^1H NMR spectra of t-butyl-, isopropyl-, and n-propyl-nitroacetylenes proved to be very simple, as expected, and contained only signals corresponding to the protons of the alkyl groups.

Table 4.

Compound	δ, p.p.m.	Δδ, p.p.m.	References
t-Bu–CH=CH_2	1.00	—	31
t-Bu–CH=$CHNO_2$	1.15	0.15	3
t-Bu–C≡CH	1.20	—	31
t-Bu–C≡CNO_2	1.34	0.14	3
t-Bu–C≡C–COOEt	1.32	0.12	3
t-Bu–C≡C–CN	1.32	0.12	3

The shifts of the proton signals of the Me_3C group in the α-position relative to the multiple bond under the influence of various electrophilic substituents (all the compounds were used as solutions in CCl_4), which are listed in Table 4, illustrate the influence of the nitro-group.

IV. CHEMICAL PROPERTIES

α-Nitroacetylenes are extremely unstable. They change on storage or heating much faster than the lower nitroalkenes[32,33], 1-nitrobuta-1,3-diene[34], and also fluoroacetylenes[35].

Under the conditions of gas–liquid chromatography (t = 107–119°C), t-butylnitroacetylene (IV) did not change, isopropylnitroacetylene (V) decomposed to the extent of 30–50%, and n-propylnitroacetylene (VI) decomposed to the extent of 80–90%.

It was found by gas–liquid chromatography and infrared spectroscopy that the half-life at room temperature is 2–3 days for compound (IV), 10 h for unpurified specimens of compound (V), and 1–2 h for compound (VI).

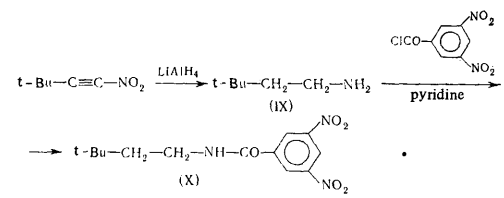
The thermal stability of compound (IV) has been studied in greatest detail. It has been shown that in 20% solution in toluene (IV) decomposes to the extent of 50% at 80–85°C in 30 min, the decomposition being almost complete after 10 h. Compound (IV) distills at 55°C/15 mmHg with partial decomposition. It melts at about −3°C.[3]

In dilute solutions in non-polar solvents (IV) is stable at 110–120°C. The type of transformation of nitroacetylenes on storage and heating has not been established.

The inductive effect of the nitro-group is very strong and comparable to the inductive effect of fluorine[36]. Therefore the oligomerisation of t-butylnitroacetylene and t-butylfluoroacetylene should presumably proceed similarly. Trifluoromethylacetylene is converted on storage into substituted benzene isomers and certain tetrameric products[37,38]. However, after standing for one month at room temperature, the products of the oligomerisation of compound (IV) contained, according to gas–liquid chromatographic data, more than 20 compounds in addition to the starting material, from which only one adduct (yield 1%) corresponding to the formula $C_{12}H_{18}N_4O_8$ (two molecules of t-butylnitroacetylene combined with an N_2O_4 molecule) could be isolated.

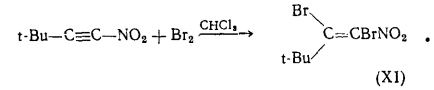
1. Hydrogenation

To demonstrate the structure of compound (IV), it was subjected to catalytic hydrogenation over platinum oxide, which yielded a mixture of the expected amine (IX) and, as shown by ^1H NMR, a dimeric compound corresponding to a symmetrically disubstituted hydrazine[3]. The reduction of compound (IV) by lithium tetrahydroaluminate in ether yielded the amine (IX), which was isolated in the form of the 3,5-dinitrobenzoyl derivative (X)[39]:



2. Bromination

The reaction of t-butylnitroacetylene with bromine in chloroform proceeds with slight evolution of heat and leads to 1,2-dibromo-1-nitroethylene in almost quantitative yield:



(XI)

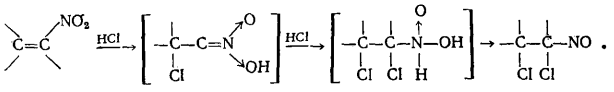
The ^1H NMR spectrum of this compound contains a singlet with δ = 1.5 p.p.m. corresponding to the protons of the t-butyl group, which is displaced to a lower field compared with the initial nitroacetylene[3].

The mechanism of this seemingly elementary reaction requires special consideration. The reaction of bromine with olefins and acetylenes is regarded as electrophilic addition[40]. However, the acceleration of the bromination of substituted tolanes (regardless of the nature of the substituents)[41] suggested that the first stage in these non-catalysed reactions involves the addition of the nucleophilic agent[42]. The situation in the case of nitro-olefins and nitroacetylenes is still more complicated owing to the possibility of acid catalysis[43] by the traces of HBr and HCl present in chloroform and responsible for the nucleophilic attack by bromine.

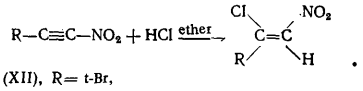
The lack of experimental data precludes the prediction of the stereochemical sequence of both the catalysed and non-catalysed additions to nitro-compounds containing multiple bonds.

3. Hydrochlorination

The interaction of nitro-olefins with anhydrous hydrogen chloride is known to involve a complex sequence of reactions[44] leading to nitro-olefins without an α-hydrogen atom, i.e. 1,2-dichloro-1-nitroisoalkanes[45]:

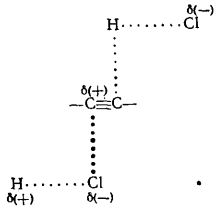


The hydrochlorination of nitroacetylenes (IV) and (V) even in the presence of an excess of HCl proceeds in a different way—with quantitative formation of *cis*-2-chloro-nitro-olefins[3]:



(XII), R= t-Bu,
(XIII), R= i-Pr.

Thus the 1,4-addition expected by analogy with nitro-olefins did not occur with nitroacetylenes. The mechanism of the addition of hydrogen chloride to nitro-acetylenes is probably different from that in the case of nitro-olefins. The *trans*-addition of hydrogen chloride to the triple bond is usually regarded as an electrophilic addition reaction, which is kinetically of third order (a reaction of the type AdE3). The transition state can be represented as follows[3]:



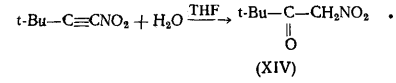
The addition of HCl to activated acetylenic systems, for example to acetylenedicarboxylates, is known to begin with nucleophilic attack[46-48] and to end with rapid protonation. Since nitroacetylenes should be still more electrophilic systems, in this case addition probably proceeds via the same mechanism.

4. Hydration

Water causes the polymerisation of lower nitro-olefins[44,49,50]. By selecting conditions eliminating polymerisation, it was possible to achieve the addition of water to the double bond with subsequent cleavage of the addition product into a carbonyl compound and a nitroalkane. Under alkaline conditions, this reaction is reversible, resulting in the formation of an aldol. The reaction is of the retroaldol type[51,52].

When nitroethylene was treated with a cold dilute sulphuric acid solution, the intermediate nitroalcohol was isolated[53].

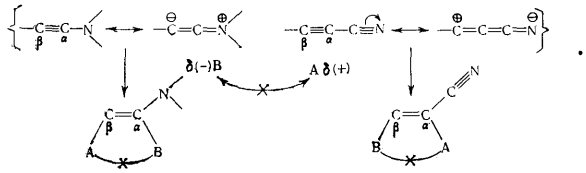
t-Butylnitroacetylene is hydrated much more readily than nitro-olefins and is smoothly converted under mild conditions (tetrahydrofuran, 20°C, 24 h) into 3,3-dimethyl-1-nitrobutan-2-one (XIV)[3]:



(XIV)

5. Nucleophilic Addition

By analogy with nitroalkenes, it was to be expected that nitroacetylenes would tend to undergo nucleophilic addition reactions. Substituted acetylenes conjugated with nucleophilic and electrophilic groups differ in the order in which nucleophiles add to them:



The similarity of the electrophilic properties of the nitro-group and fluorine can be extended also to the chemical behaviour of nitro- and fluoro-acetylenes[54]. The closeness of the electronegativities of the nitro-group and fluorine follows from a comparison of the chemical shifts in the ^{1}H NMR spectra of the M–X systems associated with the electronegativity of the substituent X (Table 5) and also from a study[37] in which the electronegativities of the organic functional groups were calculated from the chemical shifts and the coupling constants of 5-endo-substituted norbornenes.

Table 5. The chemical shifts of the protons in Me–X (solvent CCl_4).[3]

X	NO_2	F	Cl	$Me_2\overset{\oplus}{N}$	CN	H
δ p.p.m.	4.72	4.67	3.46	3.33*	2.32	0.13**

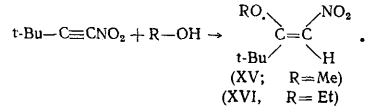
*In CF_3COOH.
**Gas.

The addition of alcohols and amines. α-Nitroacetylenes exhibit a marked electrophilic reactivity The reactions of t-butylnitroacetylene (IV), which is the most stable of the α-nitroacetylenes investigated, with nucleophilic agents proceed without catalysts at temperatures between −30° and 20°C. The electrophilic properties of the triple bond in this compound are much more pronounced than those of the triple bond in the heterosubstituted acetylenes of analogous structure[55] and the double bond in their ethylene analogues[56-58].

It has been shown that, under mild conditions (room temperature, 24 h, no catalyst) in methanol and ethanol, compound (IV) is smoothly converted into the corresponding *cis*-nitrovinyl ethers (yield 95%).

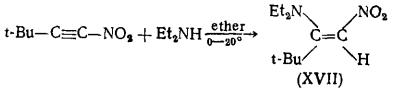
The enhanced intensity of the infrared bands of the double bond (1615, 1618 cm^{-1}) confirms the occurrence of

unhindered conjugation of the double bond with the nitro-group, which is possible only in the *cis*-form of the nitro-vinyl ether[3]:



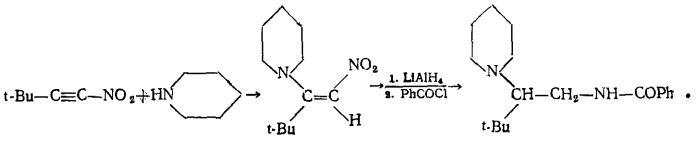
(XV; R=Me)
(XVI, R=Et)

It is known that ammonia and primary and secondary aliphatic amines readily add to nitro-olefins[49] and also cause their polymerisation[50]. The reaction of compound (IV) with aliphatic amines is exothermic and reaches completion with inflammation. However, the reaction with diethylamine in ethereal solution under controlled conditions gives rise to high yields of the expected adducts[3]:



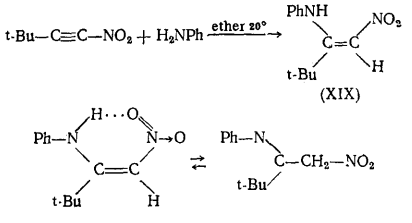
(XVII)

The product of the addition of piperidine to compound (IV) was not isolated in a pure form, but was identified as the benzoyl derivative of its hydrogenation product (XVIII):



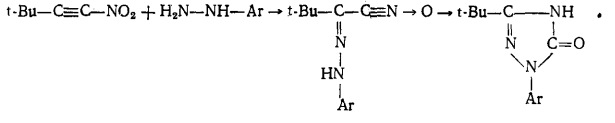
(XVIII)

The reaction with aniline is accompanied by the formation of the normal *trans*-addition product (XXa), which is in equilibrium with its tautomer (XXb)[3]:



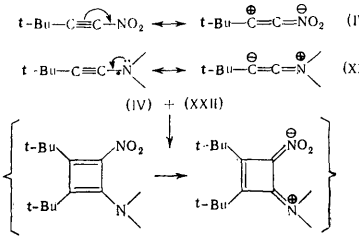
(XXa) (XXb)

Viehe and coworkers[59] showed recently that the reaction of compound (IV) with arylhydrazines results in the formation of 1,3-disubstituted 1,2,4-triazolin-5-ones (XXI):



(XXI)

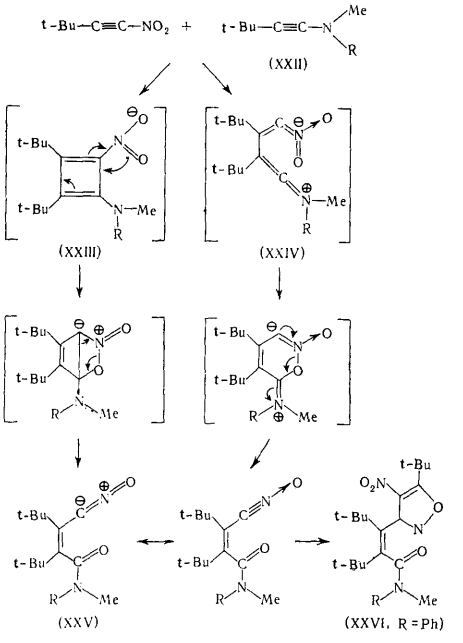
The high and opposed polarisations of t-butylnitro- and amino-acetylenes suggested the possibility of a direct combination of these compounds into the cyclobutadiene system via the mechanism:



The attempts at the synthesis of such systems on the basis of α-nitroenamines, undertaken by Breslow et al.,[60] were unsuccessful.

On the other hand, according to infrared spectroscopic data, the reaction of compound (IV) with (XXIIa) proceeds quantitatively with formation of compound (XXVa) (Scheme 1), which, however, could be isolated in only 29% yield. Compound (XXVc) was isolated similarly (in 21% yield); in this case there is in addition a competing reaction involving the 1,3-dipolar addition of compound (IV) to (XXVb), leading to the formation of an isoxazole derivative (XXVI)[3].

Scheme 1 (Ref.3)

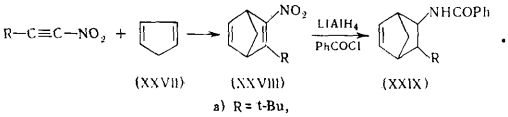


(XXII)-(XXV): a) R=Me; b) R=Ph.

6. Diels–Alder Reactions

The rate of Diels–Alder reactions is known to increase following the introduction of electron-donating substituents into the dienes and of electron-accepting substituents into the dienophiles (the "Alder rule")[61,62]. On this basis, it was possible to postulate that, when the t-butyl group in compound (IV) does not give rise to steric hindrance, the 1,4-cycloaddition of compound (IV) will be facilitated in the case of electron-rich alicyclic dienes.

However, among a large class of dienes [2,3-dimethylbuta-1,3-diene, cyclopentadiene(CPD), cyclohexa-1,3-diene, cyclohepta-1,3-diene, cyclo-octatetraene, tetracyclone, furan, 2,5-dimethylfuran, and diphenylisobenzofuran] only CPD (XXVII), one of the most reactive dienes[61,62], readily reacts with (IV) and also with (V) and (VI) to form the corresponding adducts (XXVIII). The rate of formation of adducts exceeds the rate of dimerisation of CPD.



(XXVII) (XXVIII) (XXIX)

a) R = t-Bu,
b) R = n-Pr,
c) R = i-Pr.

The adducts (XXVIII) and the CPD dimer were separated by column chromatography on silica gel. Compound (XXVIIIa) was obtained in high yield in the form of a yellow liquid, which was oxidised on standing in air. Similar compounds (XXVIII, b and c) proved to be even more sensitive to air. Despite the difficulty of its purification, the product (XXVIIIb) was identified by gas–liquid chromatography and ^{1}H NMR.[3]

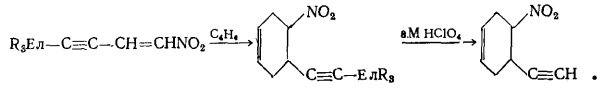
Compared with other dienophiles, nitro-olefins are known to be most reactive in relation to CPD[63,64]. However, in order to obtain information about the relative reactivity of the $-C\equiv C-NO_2$ system, it was necessary to compare, for example, compound (IV) with other acetylenic systems, the pronounced dienophilic properties of which are already known. Since the steric conditions must be the same, compounds (XXX) and (XXXI) were specially synthesised. It was shown[3] that the ratio of the rate constants for the reactions of CPD with (IV) and other members of the series

t-Bu—C≡C—NO_2 (IV); t-Bu—C≡C—COOEt (XXX); t-Bu—C≡C—CN (XXXI); t-Bu—CH=CHNO_2 (XXXII)

exceeds 10^4. The comparison of the reactivities of compound (IV) and the chloride of t-butylacetylenecarboxylic acid would probably be more instructive[3], since the determination of the rate constants for the Diels–Alder reaction of CPD (k) with *trans*-XCH≡CHX[65] and t-BuC≡CY indicates the similarity of the influence of the COCl and NO_2 substituents.

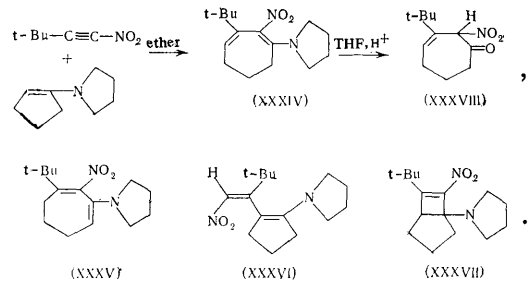
trans-X-CH=CHX					t-BuC≡CY	
Substituent X	COCl	COPh	CN	$COOMe_3$	NO_2	CN
k	6700	18	1,1	1.0	$>10^4$	1,0

4-Trialkylsilyl- and 4-trialkylgermyl-1-nitrobut-1-en-3-ynes (XXXIII) have also been used as dienophiles[11]. However, the condensation of these compounds with alka-1,3-dienes (buta-1,3-diene, CPD) involves only the olefinic group and the adducts formed are readily cleaved in an acid medium at the Si–C or Ge–C bond:



(XXXIII)

The reaction of compound (IV) with *N*-cyclopent-1-enylpyrrolidine is unusual[66]. By analogy with the reactions of enamines with nitro-olefins[67–76] and olefins containing other electrophilic substituents[67,68,77–80] and also with acetylenic systems[66,80–83], the formation of four products might have been expected in this case: a derivative of cycloheptadiene (XXXIV), its tautomer (XXXV), the Stork alkylation product (XXXVI), and a cyclobutene derivative (XXXVII):



However, the ^{1}H NMR spectrum of the resulting adduct showed the presence of the cycloheptadiene structure (XXXIV) alone. The structure of the adduct (XXXIV) was also confirmed by mild acid hydrolysis leading to the α-nitroketone (XXXVIII).

The addition of enamines to nitroacetylenes proceeds in a complex manner in a number of stages, which is confirmed by the difference between the infrared spectrum recorded immediately after the completion of the reaction and that of the product obtained after recrystallisation. An unstable product (XXXVII) is probably formed initially (the mode of addition is determined by the steric hindrance due to the *cis*-t-butyl group), and rearranges to compound (XXXIV) isolated finally. The reaction of nitroacetylenes with cyclic enamines constitutes a convenient synthetic method for the expansion of the ring by two carbon atoms[66].

The data quoted in this review demonstrate the absence of a complete analogy in the behaviour of ethylenic and acetylenic nitro-compounds. The study of nitroacetylenes has only just begun and presumably in the immediate future new interesting evidence will be obtained for the mutual influence of the atoms in compounds of this class and for the relation between their electronic structure and reactivity; also a wide variety of their synthetic possibilities will be discovered.

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Lensovet Leningrad Technological Institute