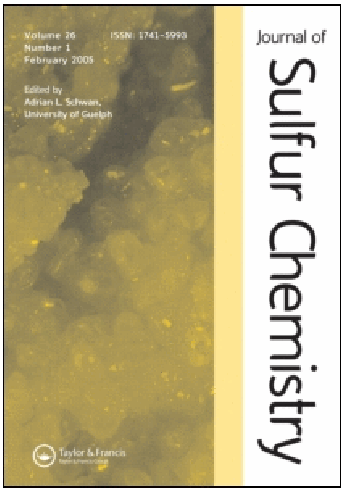

Journal of Sulfur Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926081

Conjugated 1,2- and 1,4-Nitrothio(sulfonyl)alkenes and -Dienes

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To cite this Article Pavlova, Z. F. , Lipina, E. S. and Perekalin, V. V.(1995) 'Conjugated 1,2- and 1,4-Nitrothio(sulfonyl)alkenes and -Dienes', Journal of Sulfur Chemistry, 16: 2, 149 — 170
To link to this Article: DOI: 10.1080/01961779508048737
URL: http://dx.doi.org/10.1080/01961779508048737

Sulfur Reports, Volume 16, pp. 149–172
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CONJUGATED 1,2- AND 1,4-NITROTHIO(SULFONYL)ALKENES AND -DIENES

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(Received April 19, 1993)

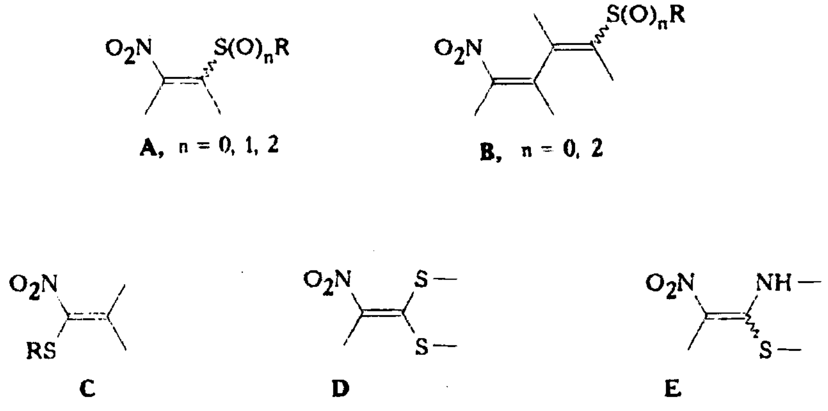
The synthesis and reactions of four groups of conjugated sulfur-containing compounds; i.e. 1-nitro-2(4)-thioethenes (and -dienes) and 1-nitro-2(4)-sulfonylethenes (and -dienes), which have become known in recent years, are discussed. Nitrothioethenes may be obtained by elimination reactions of nitrothioketals (synthesised from α-nitro ketones) and nitrohalothioethanes (synthesized from α-nitro-β-acetoxyethanes), as well as by halogen or nitro group displacement by a thio group in 1-nitro-2-halo- or 1,2-dinitroethenes. The last method was used for nitrothiodiene preparation from dinitrodienes. The stereochemistry of the thiylation of conjugated dinitro compounds is described. Nitrosulfonylethenes and -dienes can be obtained by oxidation of the corresponding nitro sulfides as well as by nitrovinylation of arenesulfinates with dinitroethenes and -dienes. Two-electron oxidation of 1-nitro-2-sulfonylethane dianions is suitable for the preparation of 1-nitro-2-sulfonylethenes. Nucleophilic displacement of the sulfur-containing group in nitrothio(sulfonyl)ethenes by amines, alkoxide and thiolate ions as well as Diels-Alder reactions are described. The spectral data (^{1}H NMR, IR, UV) of the compounds mentioned are discussed.

Key words: Nitrothioethenes, nitrothiodienes, nitrosulfonylethenes, nitrosulfonyldienes.

CONTENTS

1. INTRODUCTION

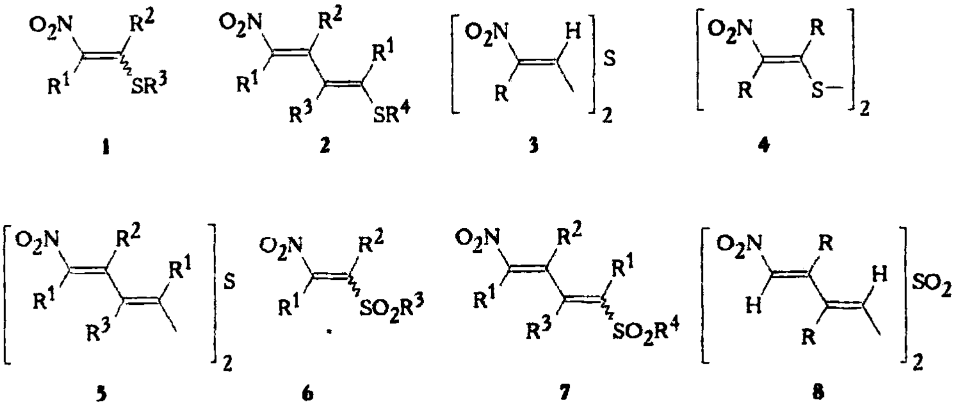
Known conjugated sulfur-containing nitro compounds are represented by the following types: **A–E** (Scheme 1).



SCHEME 1

This review is devoted to the types **A** and **B** (n = 0–2), both practically unknown until recently (1980). Such compounds are of considerable importance as new functionalized conjugated ethenes, which may be widely used for synthetic transformations to other conjugated ethenes, cyclohexenes, heterocycles and potentially biologically active substances.

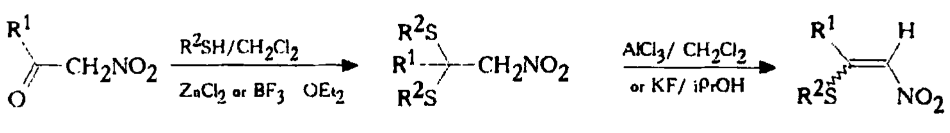
The following compounds **1–8** of group **A** and **B** have been synthesized (Scheme 2):



SCHEME 2

2. THE SYNTHESIS OF 1-NITRO-2-THIOALKENES AND 1-NITRO-4-THIODIENES

A general preparative method has been proposed for the 1-nitro-2-thioethenes from α-nitro ketones **9** via the thioketals **10** with subsequent thiol elimination. The nitrothioethenes **1** were presumably obtained in the Z-form[1,2] (Scheme 3).



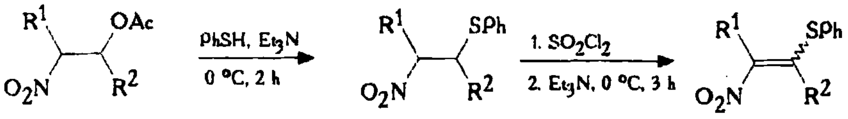
9 10 1 a - g

1	a	b	c	d	e	f	g
R^1	Me	Me	Et	Ph	Ph	3-C_6H_4Cl	4-C_6H_4COOEt
R^2	Et	Ph	Ph	Ph	Et	Et	Et
E/Z	1/2	1/9	3/7	5/95	Z	Z	Z
yield (%)	55	95	75	98	57	79	57
Ref.	1	2	2	2	1	1	1

SCHEME 3

This method used for cyclic α-nitro ketones (nitrocyclohexanone[2] and -heptanone) is limited in its scope by the impossibility to obtain β-unsubstituted nitrothioethenes due to the instability of α-nitro aldehydes.

Another method is based on the reaction of 1-nitro-2-acetoxyalkanes **11** with thiophenol in the presence of triethylamine leading to 1-nitro-2-phenylthioalkanes **12**, transformed to 1-nitro-2-phenylthioethenes **1** by chlorinatinon and dehydrochlorination as a mixture of E- and Z-isomers[3,4] (Scheme 4).

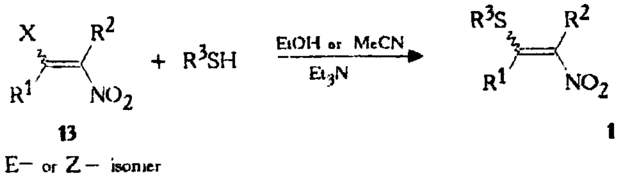


11 12 1

1	a	b	c	d	e
R^1	H	Me	H	Et	n-C_5H_{11}
R^2	H	H	Me	H	H
E/Z	95/5	1/1	1/1	1/1	1/1
yield (%)	95	95	83	88	88

SCHEME 4

A few examples of 1-nitro-2-thioethene synthesis from 1-nitro-2-haloethene[5–8] **13** or 3,4-dinitro-3-hexene[9] and arenethiols are known. The authors proposed the E-configuration[6–9] for the only isomer formed independent of the configuration of the starting material (Scheme 5):

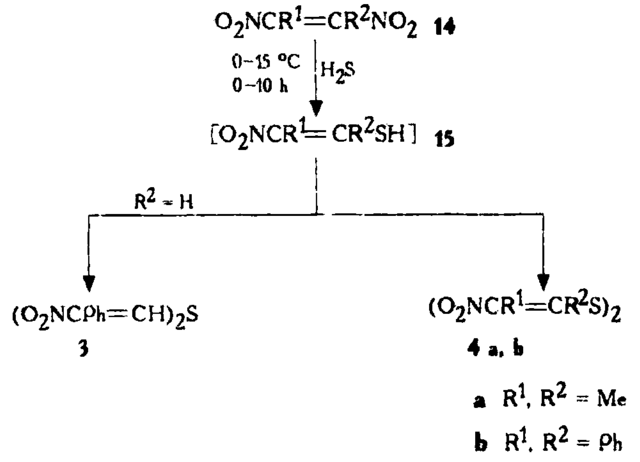


1	a	b	c	d	e	f	g
R^1	Ph	Ph	Ph	Ph	Ph	Ph	Et
R^2	H	H	Ph	Ph	Ph	Ph	Et
X	Cl	Cl	I	Cl	Cl	Cl	NO_2
R^3	CH_2Ph	4-C_6H_4Me	4-C_6H_4Me	Et	CH_2-CH_2-OH	$(CH_2)_nCOOMe$	4-C_6H_4Me

SCHEME 5

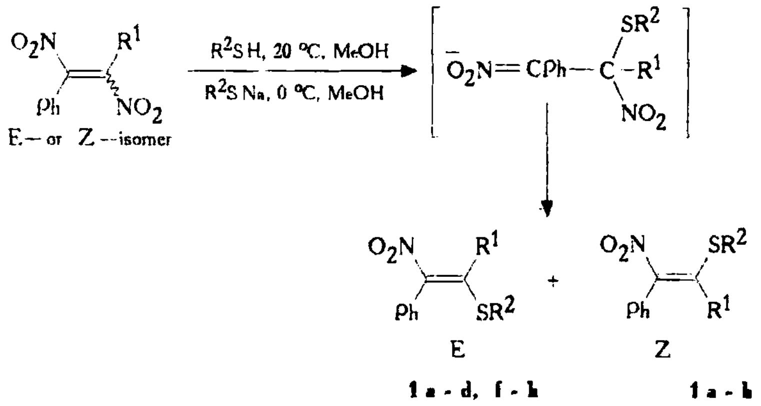
The reactions of 1,2-dinitroethenes **14** with hydrogen sulfide and alkane- and arenethiols also result in the substitution of a nitro group by a thio group, and have been thoroughly studied as a means for the synthesis of nitrothioethenes.[10-12]

The reaction with hydrogen sulfide does not stop at the step of the nitrothioethenethiol **15** and follows two main paths, depending on the structure of the starting nitroethene: monosubstituted dinitroethenes form bis(nitroalkenyl) sulfides **3** while disubstituted substrates undergo oxidation to form the disulfides **4**, as is the case with thiols (Scheme 6):



SCHEME 6

The reaction with thiols results in 1-nitro-2-alkyl(aryl)thioethenes (Scheme 7).



1	a	b	c	d	e	f	g	h
R^1	H	H	H	H	H	Ph	Ph	Ph
R^2	Ph	4-C_6H_4Me	4-C_6H_4Cl	4-C_6H_4Br	2-$C_6H_4NH_2$	4-C_6H_4Cl	Ph	4-C_6H_4Br

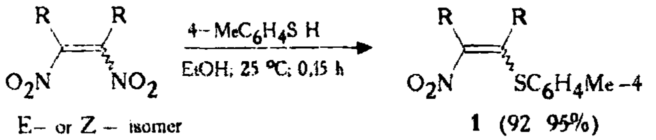
SCHEME 7

The stereochemical result of the thiylation of 1,2-dinitroethenes depends on the nature of the reagent and the structure of the starting dinitroethene.[11] In the absence of base a mixture of Z/E-isomers is formed. It has the same composition regardless of the thiylation reagent. Moreover, in reactions with dinitrostyrene the E-isomer predominates while the Z-isomer is the main product derived from a dinitrostilbene independent of its configuration (Table 1).

TABLE 1 The isomer distribution in the thiylation of dinitroethenes

$O_2NCPh{=}CR^1NO_2$		ArSH				ArSNA			
R^1	Isomer	Reaction time, h	Compound	Z/E Isomer ratio	Yield, %	Reaction time, h	Compound	Z/E Isomer ratio	Yield, %
H	E	5	**1a**	1/1.4	92				
H	E	24	**b**	1/1.6	57	1	**1b**	4/1	62
H	E	0.2	**c**	1/1.5	90	0.5	**c**	3/1	95
Ph	Z	1	**d**	1/1.5	64				
Ph	Z	15	**g**	3/1	92				
Ph	Z	10	**f**	3/1	90	0.5	**f**	Z	87
Ph	Z	11	**h**	3.5/1	65	0.7	**h**	Z	84
Ph	E	17d	**f**	Z	90	4.5	**f**	Z	94
Ph	E	25d	**h**	Z	82	4.5	**h**	Z	79

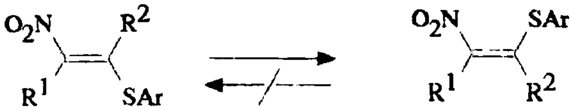
The results obtained for dinitrostilbenes are similar to those for disubstituted aliphatic dinitroethenes[13] (Scheme 8).



1 (92 95%)
a R = Me E/Z 2/3
b R = Et E/Z 1/3

SCHEME 8

In reactions of the same dinitroethenes with sodium thiolates predominantly the stablest isomer is formed. Because the Z-isomer of a dinitrostilbene reacts under significantly milder conditions than the corresponding E-isomer no isomerization of the starting dinitroethene occurs. The observed lack of stereospecifity may be due to a two-step mechanism of the reaction. Apparently, the configuration of the nitrothioethene during its reaction with thiolates is determined by the prevailing conformation of the most stable ionic intermediate. The relative stability of the isomers is confirmed by their thermal isomerization. Moreover, the Z-form is more stable.[11] (E)-1-Nitro-1-phenyl-2-arylthioethenes form a mixture of both isomers with the Z-form predominating under short-time heating. The same result is observed under catalytic conditions and in the presence of hydrogen peroxide and thiolates (Scheme 9).



SCHEME 9

The preferred formation of the Z-form is not only characteristic of sterically hindered nitro-phenylthioethenes. Unsubstituted (E)-1-nitro-2-arylthioethenes have been shown to be converted to 75% of the Z-form upon 1 h heating in MeOH. Apparently, the unusual stability of the Z-structure is due to stabilizing interaction of NO_2 and the thio group in the *cis*-position. In a recent paper[14] the possibility of an attractive interaction between these groups in the case of a certain geometry has been confirmed. The configuration of the stereoisomers was determined by analysis of the ^1H NMR spectra: by the CSST value for unsubstituted derivatives of nitroethene; by the chemical shift of the β-nitrovinyl proton for nitrostyryl sulfides and by the chemical shift of the β-phenyl ring protons for nitrostilbenes.[11]

The reaction of (Z)-1,2-dinitrostilbene with thiols (in buffered media) has been proposed for the colorimetric analysis of alkane- and arenethiols.[15]

Vinyl nucleophilic substitution of halogen and nitro group has been used for the synthesis of the nitrothio-1,3-alkadienes **16**. Thiylation of 2-nitropentachlorobutadiene, completed by β-halogen substitution as in the case of 1-nitro-2-haloethenes, has been described.[16]

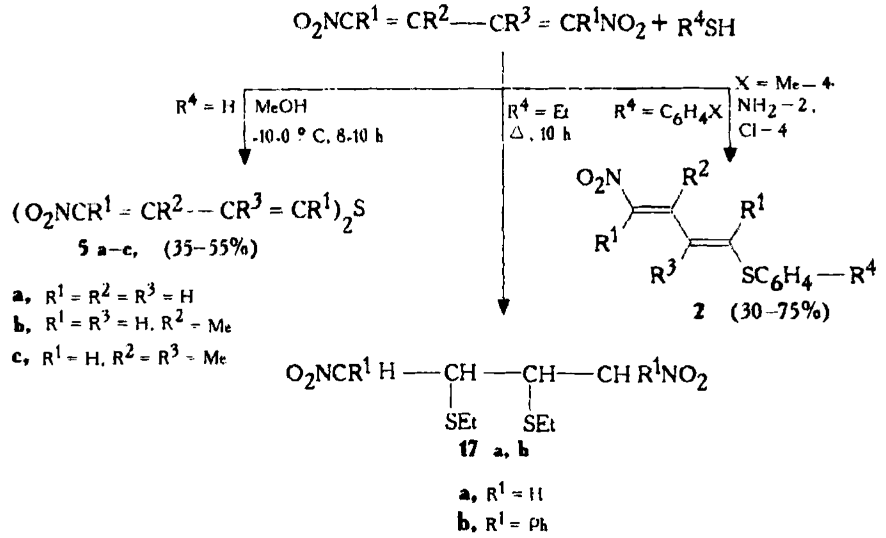
$$Cl_2C=CCl-CNO_2=CCl_2 \xrightarrow[20-25\,^{\circ}C,\ 15-17\ h]{RSH} Cl_2C=CCl-CNO_2=CClSR$$

16 (54–80%)

a, $R = C_8H_{17}$
b, $R = CMe_2Et$
c, $R = CH_2Ph$

SCHEME 10

Similar to the above-mentioned synthesis of nitrothioethenes from 1,2-dinitroethenes, 1-nitro-4-thiodienes have been obtained by thiylation of the corresponding vinylogs, the 1,4-dinitrodienes.[10,11,17,18] The reaction in this case depends on the structure of the dinitrodiene and on the nature of the reagent. In the absence of substituents on the central carbon atoms products of bis-addition to these atoms **17** are formed with ethanethiol (or ethanethiolate) in accordance with the electron density distribution in the molecule[18] (Scheme 11).



2	a	b	c	d	e	f	g	h	q
R^1	H	H	H	H	H	H	H	H	Ph
R^2	H	H	H	H	Me	Me	Me	Me	H
R^3	H	H	H	H	H	Me	Me	Me	H
R^4	Me	H	4-Cl	2-NH_2	4-Cl	Me	2-NH_2	4-Cl	4-Cl

SCHEME 11

Such a path is characteristic for the reaction of 1,4-dinitrodienes with other nucleophiles (e.g. aniline and active methylene compounds[19]). At the same time reaction with hydrogen sulfide and arenethiols occurs at the terminal atom of the conjugated system analogous to 1,2-dinitroethenes and leads to substitution of a nitro group resulting in new derivatives such as the bis(1-nitrodienyl) sulfides **5** and the nitroarylthiodienes **2**. The most vigorous reaction is with H_2S: 1,4-dinitrobutadiene forms the substitution product at -10 °C, its homolog at 0–18 °C. The reaction with arenethiols takes place at higher temperatures and use of thiolates is necessary in the case of the 1,4-dinitrobutadiene homologs.

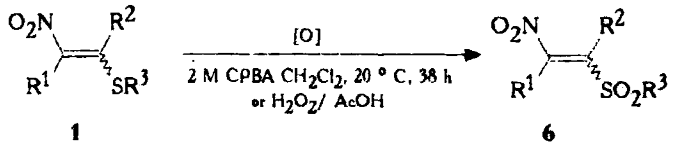
The (E,E)-structure of the nitroarylthiodienes has been determined by ^1H NMR data: by the CSST values of the vinyl group protons for unsubstituted nitrothiodienes and by the methyl proton chemical shift of the methyl homologs.[11,12]

A specific method has been proposed for the synthesis of 1-nitro-4-thiodienes: electrophilic addition of nitrobenzenesulfenyl chloride to the disodium salt of 1,4-dinitro-2,5,7-cyclooctatriene with subseqent elimination of NO_2^-.[20]

3. THE SYNTHESIS OF 1-NITRO-2-SULFONYLALKENES AND 1-NITRO-4-SULFONYLDIENES

The oxidation of organic sulfides to the corresponding sulfones by treatment with different oxidants is a well-known and convenient[21–23] method. However, until now very few examples of the synthesis of 1-nitro-2-sulfonylethenes have been reported.[9] In recent years two oxidation procedures have been proposed for this group of compounds.[4,18] Oxidation of nitrophenylthioethenes to the sulfones **6a–e** with *m*-perchlorobenzoic acid with retention of configuration has been carried out by Ono *et al.*[3,4] (Scheme 12).

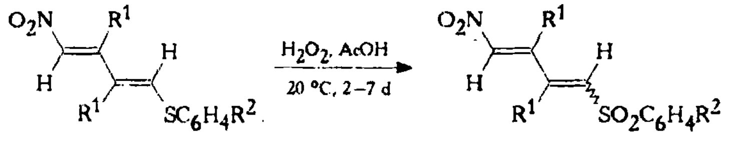
We developed a mild oxidation procedure using excess hydrogen peroxide in acetic acid at room temperature for 4–5 d to prepare the sulfones **6f–k**.[24–25]



6	a	b	c	d	e	f	g	h	i	j	k
R^1	H	Me	n-C_5H_{11}	H	Et	H	Ph	Ph	Ph	Ph	Ph
R^2	H	H	H	Me	H	H	H	H	H	Ph	Ph
R^3	Ph	Ph	Ph	Ph	Ph	4-ClC_6H_4	4-MeC_6H_4	4-ClC_6H_4	4-BrC_6H_4	Et	4-ClC_6H_4
E/Z	E	1/1	1/1	1/1	1/1	E	E	1/2	1/2		E
yield	53	88	88	87	86	47	57	62	66	90	90

SCHEME 12

This method has been applied to the above-mentioned 1-nitro-4-arylthio-1,3-butadienes which allowed to obtain a new group of compounds, the 1-nitro-4-arylsulfonyl-1,3-butadienes[25] **7** (Scheme 13).



2 → 7

7	a	b	c	d
R^1	H	Me	Me	Me
R^2	4-Cl	4-Cl	4-Me	2-NH$_2$

SCHEME 13

The oxidation of unsubstituted 1-nitro-2-arylthioethenes and of their 1-phenyl homologs as well as of the (E,E)-isomers of 1-nitro-4-arylthiodienes proceeds with retention of configuration. One exception is the unsubstituted 1,4-nitroarylsulfonyl-1,3-butadiene, obtained from the (E,E)-thiodiene and isolated as a mixture of (E,E)- and (Z,Z)-isomers in a 2:1 ratio, the last did not isomerize upon prolonged heating. An increased amount of oxidant and prolonged reaction time in the case of the nitrostyrenes leads to mixtures containing most of the Z-form (E:Z = 1:2). In contrast, only the E-isomer of nitrosulfonylstilbene was obtained from the Z-isomer of nitrothiostilbene. These stereochemical results may be explained by isomerization of the primary oxidation products to more stable forms, as shown in model experiments.

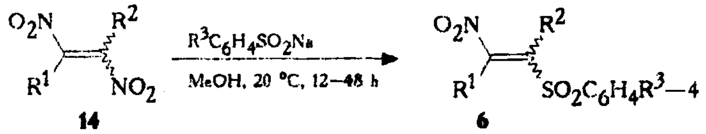
The oxidation of the bis(1-nitrodienyl) sulfides **5** requires more forcing conditions and leads to the bis-(1-nitrodienyl) sulfones **8** (Scheme 14).[25]

$$\underset{\mathbf{5}}{(O_2NCH{=}CR^1{-}CR^2{=}CH)_2S} \xrightarrow[50\ ^\circ C,\ 7-18\ h]{H_2O_2/AcOH} \underset{\mathbf{8}\quad (40-55\%)}{(O_2NCH{=}CR^1{-}CR^2{=}CH)_2SO_2}$$

8	a	b	c
R^1	H	H	Me
R^2	H	Me	Me

SCHEME 14

The nitrovinylation of arenesulfinates is another method for the synthesis of unsaturated nitro sulfones. Four such derivatives have been obtained by reaction of 1-nitro-2-chloroethene with arenesulfinates.[26-27] The reaction with styrylsulfinates leads to nitro(divinyl) sulfones.[28] We proposed 1,2-dinitroethenes and 1,4-dinitrodienes as nitrovinylation reagents. They react with sodium sulfinates at room temperature. The corresponding reaction of dinitroethenes proceeds via substitution of a nitrogroup to give 1-nitro-2-sulfonylethenes (Scheme 15).[25]

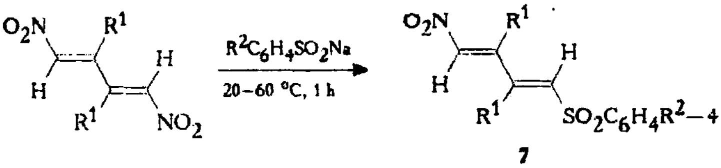


6	a	b	c	d
R^1	Ph	Ph	Me	Ph
R^2	H	H	Me	Ph
R^3	Me	H	Me	Me

SCHEME 15

As in the case of thiolates reaction with arenesulfinates results in the formation of one isomer (Z or E) independent of the initial configuration of the nitroethene.

The reaction of 2,3-disubstituted 1,4-dinitro-1,3-dienes with sodium arenesulfinates occurs at the terminal carbon atom of the diene system to give the 1-nitro-4-arylsulfonyldienes 7 (Scheme 16).

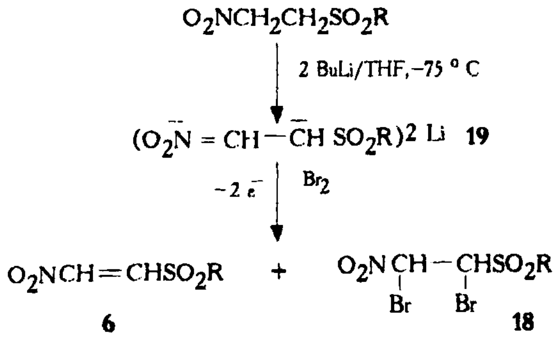


7	a	b
R^1	Me	Ph
R^2	H	Me

SCHEME 16

However, this method failed to give an unsubstituted nitrodiene, 1-nitro-4-arylthio-1,3-butadiene: even in the absence of base the reaction with benzenesulfonic acid at 0–15 °C led to resinification and the reaction products were not identified.

A previous synthesis of the nitrosulfonylethenes **6** involved oxidative introduction of a double bond in α,β-diactivated ethanes.[29–31] It involves two-electron oxidation of the corresponding conjugated dianions with bromine. A series of 1,2-dinitroethenes **14** (from 1,2-dinitroalkanes)[29] and tetrasubstituted ethenes (R = CN, COR, COOR)[30] has been prepared by this method. The oxidation products **6** as well as the dibromides **18** are formed upon treatment of the dianions **19**, obtained from 1-nitro-2-sulfonylethanes, with bromine (Scheme 17).[31]



6	a	b	c
R	Et	4-MeC_6H_4	4-ClC_6H_4

SCHEME 17

4. SPECTROSCOPY OF NITROTHIO(SULFONYL)ALKENES AND -DIENES

The characteristic electronic structure of the two groups of sulfur-containing nitroethenes is determined by the presence of an electron donating sulfide sulfur in one and an electron accepting sulfonyl group in the other, both conjugated with the nitrovinyl moiety. In the first case a considerable bond polarization by p,π-interaction is to be expected while in the other the polarization is less pronounced than the high electrophilicity of the ethylene bond. These properties are reflected in the spectral characteristics as compared with those of nitroethenes. In the NMR spectra of nitrothioethenes the chemical shift of the β-vinyl protons is observed at low field and the significant $\Delta\delta$ for the E-isomers of nitroethenes of 1.20–1.56 ppm reflects the strong polarization of the C=C bond while for the corresponding parent nitroethenes this value is 0.25–0.44 ppm (Table 2)*. These differences are the same for E- and Z-nitroarylthioethenes with substituents on the benzene ring (X = 4-CH_3, 4-Halo) while the chemical shifts change considerably.[11]

---

* Spectral data for unsubstituted nitrothioethenes and nitrodienes are given in Tables 2, 3, 6 and 8. Data for homologs are given in the quoted papers. The conclusions presented in this paper are of general validity.

TABLE 2 1-Nitroethenes[33] and 1-Nitro-2-thioethenes[11]
$O_2NCR^1{=}CHR^2$

R^1	R^2	Configuration	^1H NMR ($CDCl_3$), δ/ppm R^1	R^2	UV ($CHCl_3$) λ_{max}, nm (ε)
H	Et	E	6.92	7.21	234 (8800)[a]
H	Ph	E	7.58	8.02	227 (8100), 309 (17200)
		Z	6.93	6.71	223 (10000), 306 (6000)[34]
Ph	Ph	E	7.30	8.23	228 (12800), 314 (13400)
		Z	7.32	7.46	282 (23300)
H	SEt	E	17.00	8.20	225 (3800), 312 (11600)
H	SPh	E	6.59	8.15	250 (8000), 312 (9850)
		Z	7.37	7.04	246 (6500), 327 (10100)
Ph	SPh	E	7.38	8.37	253 (9600), 355 (10500)
		Z			247 (12200), 345 (7300)

[a] EtOH

The chemical shifts of the diene protons correlate with the electronic structure of the substituents and high polarizability of the sulfide sulfur (Table 3).

TABLE 3 1-Nitro-1,3-butadienes[33–35] and a 1-Nitro-4-thio-1,3-butadiene[36]
$O_2NCH_A{=}CH_B{-}CH_C{=}CH_DR$

	^1H NMR ($CDCl_3$), δ, ppm				IR ($CHCl_3$) ν (cm^{-1})			UV ($CHCl_3$)
R	H_A	H_B	H_C	H_D	C=C (A)[a]	NO_2 [as] (A)	NO_2 [s] (A)	λ_{max}, nm (ε)
H					1643 1600	1525 (1.90)	1350 (2.50)	226 (6000) 280 (15200)
Ph	7.15	7.97	6.64	7.34	1638	1522 (2.03)	1342 (5.20)	288 (11350) 365 (24400)
SC_6H_4 Me	7.01	7.63	5.94	7.11	1605 (2.17)	1500 (0.92)	1326 (3.60)	260 (6100) 380 (14300)

[a] The value of A is given in $mol^{-1}cm^{-1}\cdot 10^{-4}$

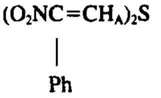
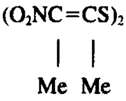
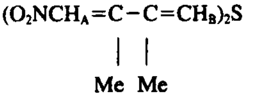
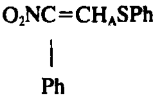
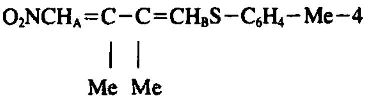
In the IR spectra of nitrothioethenes the main absorption bands are observed at 1620–1570 cm^{-1} ($\nu_{C=C}$), 1525–1490 cm^{-1} ($\nu_{NO_2}{}^{as}$) and 1330–1300 cm^{-1} ($\nu_{NO_2}{}^{s}$). Compared to structurally analogous nitroethenes[33–34] these bands are shifted to lower frequencies, while $\nu_{NO_2}{}^{s}$ and especially $\nu_{NO_2}{}^{s}$ are characterized by higher intensities (Table 4). The same trends are observed with nitrothiodiene spectra vs. nitrodiene spectra.

TABLE 4 Main IR Absorption Bands of Nitrothioethenes and Nitroethenes

Parameters	$EtCH{=}CHNO_2$	$PhCH{=}CHNO_2$	$EtSCH{=}CHNO_2$	$PhSCH{=}CHNO_2$
$\nu_{C=C}$, cm^{-1}	1650	1640	1580, 1570	1590, 1570
$\nu_{NO_2}{}^{as}$, cm^{-1}	1540	1530	1505, 1490	1490
$\nu_{NO_2}{}^{s}$, cm^{-1}	1350	1320	1300	1300
$A_{C=C}$	0,1	0,6	2,4; 1,8	5,1
$A_{NO_2}{}^{as}$	1,8	1,5	0,5	0,7
$A_{NO2}{}^{s}$	1,1	3,1	3,1	3,7

The introduction of substituents into the nitrovinyl moiety leads to decreased intensity of the $A\nu_{NO_2}{}^{s}$ and especially the $A_{C=C}$ bands.[32,35] Note the higher intensity of these bands for *bis*(nitrovinyl) sulfide and especially for *bis*(nitrodienyl) sulfide compared to the corresponding nitrovinyl and nitrodienyl sulfides (Table 5).

TABLE 5 Bis(nitrovinyl) and Bis(nitrodienyl) Sulfides, and a Bis(nitrovinyl) Disulfide

		^1H NMR ($CDCl_3$), δ, ppm		IR ($CHCl_3$), ν, cm^{-1}			
Compound		H_A	H_B	C=C (A)	$NO_2{}^{as}$	$NO_2{}^{s}$ (A)	UV ($CHCl_3$) λ_{max}, nm, (ε)
 $(O_2N\underset{\displaystyle Ph}{C}{=}CH_A)_2S$	(E)	8.28	—	1620 (1.1) 1595 (1.2)	1530 1550	1325 (6.3)	247 (10000) 380 (14300)
 $(O_2N\underset{\displaystyle Me}{C}{=}\underset{\displaystyle Me}{C}S)_2$		—	—	1595 (2.3)	1500– 1490	1310 (4.8)	352 (12500)
 $(O_2NCH_A{=}\underset{\displaystyle Me}{C}{-}\underset{\displaystyle Me}{C}{=}CH_B)_2S$		7.08	6.81	1605 (4.1)	1520	1335 (12)	250 (12000) 400 (27600)
 $O_2N\underset{\displaystyle Ph}{C}{=}CH_ASPh$	(E)	8.4	—	1640 (0.5) 1610 (0.8)	1530	1320 (2.8)	253 (9600) 355 (10500)
 $O_2NCH_A{=}\underset{\displaystyle Me}{C}{-}\underset{\displaystyle Me}{C}{=}CH_BS{-}C_6H_4{-}Me{-}4$	(E,E)	7.04	6.86	1584 (2.03)	1505	1322 (3.16)	264 (9750) 383 (15000)

This fact, together with the bathochromic shift in the UV spectra of the former may be regarded as evidence of a positive bridge effect of the sulfide sulfur. The greatest differences between nitroethenes and nitrothioethenes are observed in the absorption spectra (Table 2). The nitrothioethene spectra have two bands in the regions 225–260 and 310–360 nm. The high-energy band may be interpreted as a local excitation of the π-electrons of the conjugated system $-CH{=}CH{-}S{-}Ph$ (the maximum for diphenyl sulfide is 250 nm, ϵ = 12300). The low-energy band (due to intramolecular charge transfer in the nitro group in accordance with significant solvatochromism) stems from a transition in the group $-S{-}CH{=}CH{-}NO_2$. The absence of a band shift upon a change of substituent in the aromatic nucleus may be explained by facile rotation around the $-S{-}C_6H_4{-}X\text{-}4$ bonds. The spectra of 1-nitro-4-arylthio-1,3-dienes (λ_{max} 240–270 nm, ϵ 6000–11000 and λ_{max} 380–400 nm, ϵ 10000–20000) are characterized by a significant bathochromic shift and a hypsochromic effect on the low-energy band. The analogous influence of $-S{-}Alk(Ar)$ and Ph groups on the spectroscopic characteristics of nitrovinyl and nitrodienyl moieties should be noted (Tables 2 and 3).

The analysis of the spectral data of nitrothioethenes as a function of structure then carried out for the analogous 2-alkoxy(2-amino)-1-nitroalkenes and 1-nitro-1-butene indicates an effective p,π-interaction in these β-substituted unsaturated nitrogen compounds (Table 6).

TABLE 6 Comparison of the Spectral Data of Nitroethenes

	UV (hexane)		IR ($CHCl_3$)	
Nitroethene	λ_{max} nm	(ϵ)	$\nu_{C=C}$ cm^{-1}	A
$EtCH{=}CHNO_2$	234	(8800)	1650	0.3
$EtOCH{=}CHNO_2$	265	(10000)	1630,1570	3.7
$EtSCH{=}CHNO_2$	312	(11600)	1580,1570	4.0
$(Me)_2NCH{=}CHNO_2$	350	(22600)	1615	6.9

A comparison of the $A_{C=C}$ values allows an estimate of the donor ability of the heteroatom in the vinyl moiety; it increases in the order O < S < N. The unusual (in comparison with other β-substituted thioethenes) effect of this interaction in comparison with that in the alkoxy analogs could be due to conjugation with a powerful electron acceptor group such as the NO_2 group. In the absence of such a substituent in the vinyl group the electron donor ability increases in the order S < O < N.[37,38]

In the NMR spectra of the nitrosulfonylethenes and -dienes the β-vinyl proton resonates at higher field compared to nitrothioethenes and nitrothiodienes (Tables 7 and 8) as a consequence of the weak polarization of the C=C bond.[25,32]

With the nitro sulfones the difference between the chemical shifts of the vinyl protons (Δδ) decreases due to leveling of the electron density. In the IR spectra of the nitrosulfonylethenes the $\nu_{C=C}$ band intensity is lower than that for nitroethenes and much lower than that for nitrothioethenes with an additional difference in the shift of both nitro group bands in the direction of higher energies.

The difference between the two groups of unsaturated nitrogen compounds is due to the level of conjugation and is observed in the UV spectra (Tables 6, 8, 5 and 7).

TABLE 7 Nitrosulfonylalkenes[25,32] $O_2NCR^1{=}CR^2SO_2C_6H_4Cl\text{-}4$

			^1H NMR ($CDCl_3$), δ, ppm			IR ($CHCl_3$) ν, cm^{-1}			UV
R^1	R^2	Configuration	R^1	R^2	C_6H_5	C=C (A)	NO_2^{as}/NO_2^{s} (A)	SO_2^{as}/SO_2^{s} (A)	λ_{max}, nm (ε)
H	H	E	7.22	7.33		1620	1560 (1.9)	1345 (1.0)	253 (7000)
						(0.04)	1335 (0.7)	1160 (1.8)	
		E	7.40	7.74	7.29,	1630	1545 (2.5)	1340	265^{sh} (8000)
Ph	H				7.46	(0.1)	1325	1160(2.6)	
		Z	7.34	6.57	7.49,	1640	1550	1370	
					7.86		1340	1167	

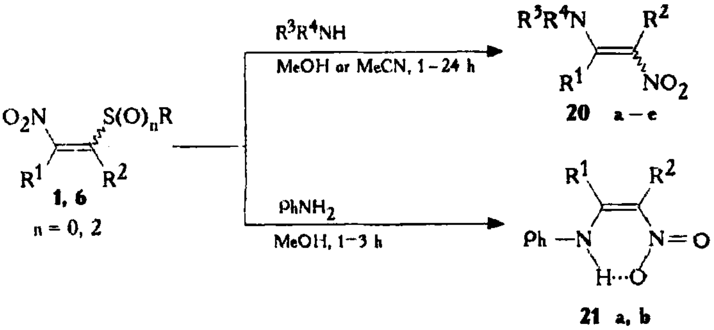
TABLE 8 1-Nitro-4-(4-chlorophenylsulfonyl)butadiene[25,32]

	^1H NMR ($CDCl_3$), δ, ppm, J (Hz)					IR ($CHCl_3F$) ν, cm^{-1}					UV
Configuration	H_A	H_B	H_C	H_D	Ph	C=C (A)	NO_2^{as} (A)	NO_2^{s} (A)	SO_2^{as} (A)	SO_2^{s} (A)	λ_{max}, nm (ε)
E, E	7.34	7.47	6.95	7.26	7.49	1640	1540	1340	1350	1155	290 (18800)
	J_{AB}	13.5	J_{CD}	14.5	7.80	(0.1)	(2.5)	(3.4)	(1.9)	(3.1)	
		J_{BC}	13.5			1590					
						(0.7)					
Z, Z	7.13	7.48	7.48	7.13	7.28	1670	1505	1340	1350	1150	265 (13500)
	J_{AB}	8.5	J_{CD}	8.5							

5. CHEMICAL TRANSFORMATIONS OF NITROTHIOALKENES AND -DIENES AND NITROSULFONYLALKENES

Nucleophilic substitution is characteristic of α-nitro-β-thio(sulfonyl)ethenes as well as of other β-functional derivatives of nitroethenes with nucleofugal substituents.

Nitrothioethenes and nitrosulfonylethenes react readily with nucleophiles such as amines to give nitroenamines[20,21,39,40] by displacement of the sulfur-containing group by an amino group (Scheme 18).



20	a	b	c	d	e
R^1	H	H	H	H	H
R^2	H	H	H	H	H
R^3	$(CH_2)_4$	Me	H	Me	$CH_2=CH-CH_2$
R^4		Me	t-Bu	Ph	$CH_2=CH-CH_2$

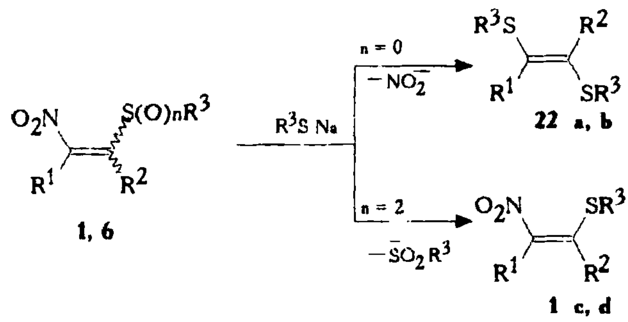
21	a	b
R^1	H	Ph
R^2	Ph	Ph

SCHEME 18

Kamimura and Ono[39] consider this reaction as a convenient method for the synthesis of nitroenamines (yields 48–85%). According to our data the reaction with aniline gives the Z-product, stabilized by an intramolecular hydrogen bond, independent of the configuration of the starting ethene. The significant reactivity of nitrosulfonylethenes should be noted.[40]

The results of kinetic studies of the reaction of 1-nitro-2-ethylthiostilbene with piperidine, carried out by Rappoport *et al.*[8], are in agreement with an addition-elimination mechanism, accepted for nucleophilic vinylic substitution reactions with highly activated substrates.

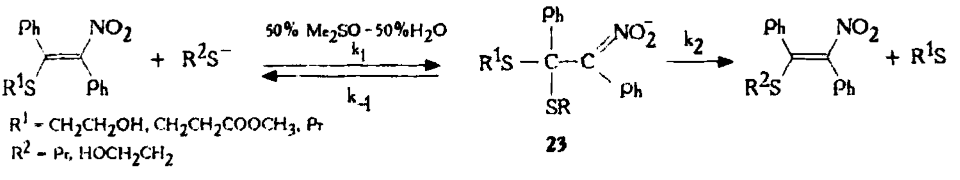
Unlike the reaction with amines, common for sulfides **1** and sulfones **2**, their behavior in reaction with ionic nucleophiles[25] (arenethiolate ions) differs: nitrosulfonylethenes give the products of the substitution of the SO_2Ar group, while ntrothioethenes react via displacement of the nitro group[40] (Scheme 19):



22, 1	a	b	c	d
R¹	H	Ph	Ph	Ph
R²	H	H	H	Ph
R³	Ph	4-Cl-C_6H_4	4-Cl-C_6H_4	4-Cl-C_6H_4
n	0	0	2	2

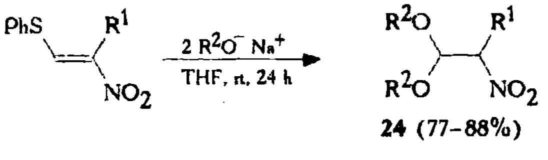
SCHEME 19

Nucleophilic substitution of (Z)-nitrosulfonylstilbene occurs readily while (Z)-nitrothiostilbene does not react with arenethiolates, even upon prolonged boiling. In the reaction of (E)-β-thio derivatives of α-nitrostilbene with aliphatic thiolate ions in a few cases spectrophotometric detection of the intermediate **23**,[7] which is usually postulated in nucleophilic vinylic substitution reactions, was possible.



SCHEME 20

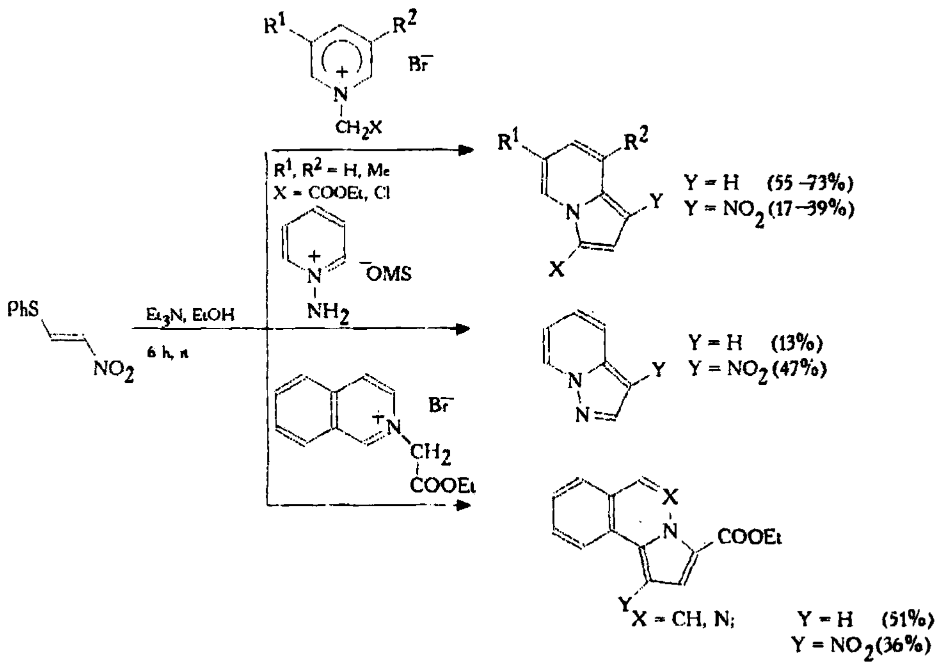
Reactions with alkoxide ions do not stop at the step of the substitution product: a second alkoxide ion adds to the latter to form a 1,1-dialkoxy-2-nitroalkane (Scheme 21).[41]



24	a	b	c	d	e
R¹	H	H	Me	Et	$n\text{-C}_7H_{15}$
R²	Me	$PhCH_2$	$PhCH_2$	$PhCH_2$	$PhCH_2$

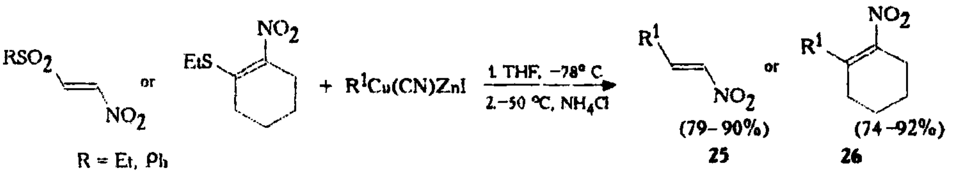
SCHEME 21

This reaction constitutes a new facile method for the preparation of α-nitro aldehyde acetals. Michael reactions of 1-nitro-2-phenylthioethylene with specific donors such as *N*-pyridinium, phthalazinium, and isoquinolinium salts are useful in heterocycle synthesis. In particular, it is an efficient reagent for the preparation of indolizine and pyrazolopyridine derivatives (Scheme 22).[42]



SCHEME 22

The reactions with organometallics also involve addition-elimination to give products of thio or sulfonyl group substitution (Scheme 23).



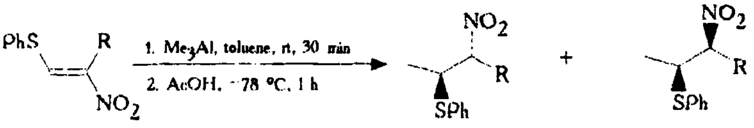
25 R^1= $(CH_2)_3COOEt$, $(CH_2)_3CN$, (E)-CH=CH(Hex), (Z)-CH=CH(Bu), $CH(OAc)CH(CH_3)_2$, $CH(OAc)(CH_2)_3OPiv$, CH(OAc)Pent, $(CH_2)_4OOCCH{=}CHPh$-(E)

26 R^1= $(CH_2)_3COOEt$, $(CH_2)_3CN$, $(CH_2)_3P(O)(OEt)_2$, (E)-CH=CH(Hex)

SCHEME 23

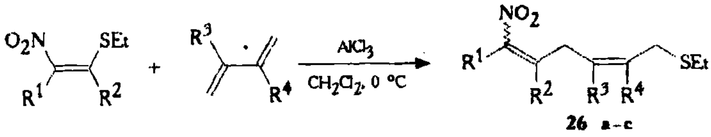
This reaction has been proposed for the highly stereoselective synthesis of functionalized nitroethenes **25**, **26** and nitrodienes.[43]

However, the reaction of 1-nitro-2-phenylthioethenes with Me_3Al results in the products of addition;[44] the reaction is stereoselective:



SCHEME 24

1-Nitro-2-thioethenes are recommended as reagents for the regio- and stereoselective 1,4-functionalization of 1,3-dienes under the influence of aluminum chloride with formation of (Z)-ethenes.[45,46]



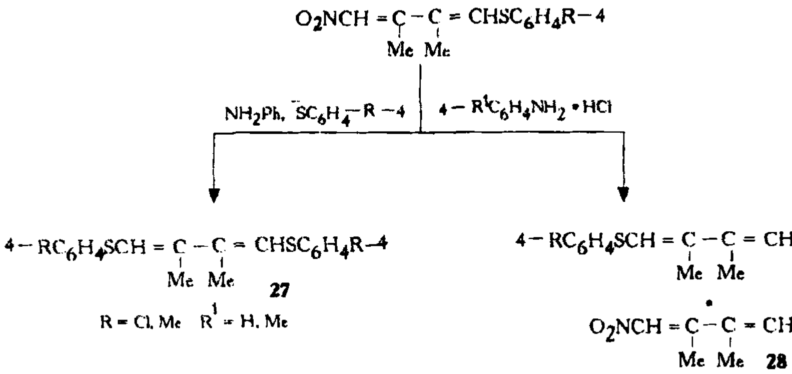
26 a–c

26	a	b	c
R^1	$(CH_2)_n$	H	Me
R^2	$(CH_2)_n$	Me	C_6H_{13}

SCHEME 25

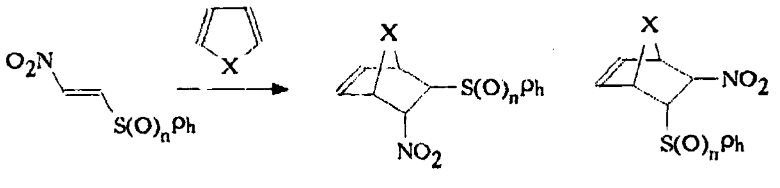
The chemical behavior of 1-nitro-4-arylthiodienes has only been studied vis-a-vis amines: they react very vigorously with aniline; however, the products formed, the 1,4-bis(arylthio)dienes **27** and their complexes **28** with the starting nitrothiodiene **2** have been identified only in the case of 2,3-disubstituted nitrothiodienes.

The formation of **27** may be caused by reaction of the starting compound with arenethiolate ion (ArS^-); this is confirmed by isolation of the same product from the reaction of **2** with arenethiolates (Scheme 26).[47]



SCHEME 26

Being electron-deficient compounds, 1-nitro-2-arylthioethens and especially 1-nitro-2-arylsulfonylethenes, are active dienophiles. Both give adducts with cyclodienes (Scheme 27), which have mostly the endo structure **29**.[3,4]

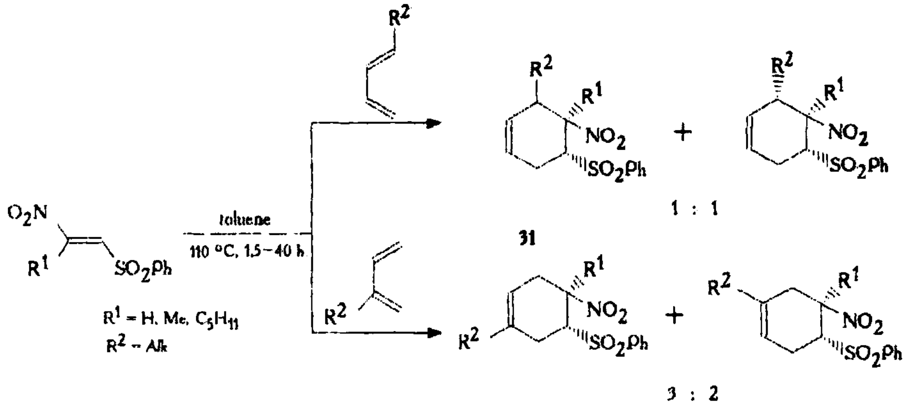


29 endo **30** exo

X = O, CH_2 (20°C, CH_2Cl_2, 0.5 h)
X = $(CH_2)_2$, $CH{=}CH{-}CH_2$ (110°C, toluene, 1.5 h)

SCHEME 27

In the presence of one phenyl group (1-nitro-2-arylsulfonyl-1-phenylethenes), the reaction slows down (58% adduct has been formed after 2 d) and the diphenyl homolog does not react at all.[48] Note the unreactivity of nitrothioethenes in reactions with aliphatic dienes.[4] The corresponding reactions of 1-nitrosulfonylethenes where a wide range of adducts **30** and **31** of cyclic and aliphatic dienes is obtained under relatively mild conditions, have been studied carefully.[49] The regioselectivity of the additions to unsymmetrical dienes should be noted (Scheme 28).



SCHEME 28

The easy reductive elimination of the nitro and sulfonyl groups (the formation of 1,4-cyclohexadienes) makes these dienophiles the synthetic equivalents of the less reactive (in these reactions) alkynes.

Thus, β-nitrothio(sulfonyl)ethenes are good Michael acceptors and react with various nucleophiles with substitution of their sulfur-containing group, but their major synthetic utility is by virtue of their dienophilic activity, which allows the synthesis of a range of carbocyclic compounds. The orienting effect of the nitro group in the Michael addition and Diels-Alder reactions prevails over that of the sulfur functional groups. Considering also the ease with which nitro compounds can be transformed into a variety of diverse functionalities, it is certain that these nitroethenes will find extensive application in chemo- and stereoselective synthesis.

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