112. Nitrosoalkenes: Synthesis and Reactivity

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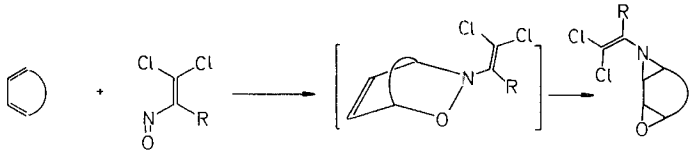
Summary

Some α- and β-halonitrosoalkenes **1** have been synthesized and characterized. The halogen atoms of the oxime precursors **2** can be substituted by alkoxy groups. Two kinds of cycloaddition reaction of **1** have been observed: i) reaction of the NO group with dienes gives 3,6-dihydrooxazine derivatives **6** which isomerise to epoxyepimines **7** in most cases of β-substituted nitrosoalkenes; ii) if 4,5-dihydrooxazines **22** are obtained, the cycloaddition of the nitrosoalkenes as 4π-component is presumed.

Nitrosoalkenes possess a large synthetic potential, since they comprise both an alkene activated by an electron withdrawing group and an 1,3-diene system. Furthermore, the nitroso group itself reacts with a wide number of reagents [1] and allows an easy, simultaneous incorporation of nitrogen and oxygen by addition reactions (*Diels-Alder* [2], ene-reaction [3] and (2+2)-cycloaddition [4]). However, despite the obvious interest of nitrosoalkenes, the first to be isolated (nitrosocyclohexene) was reported only in 1967 [5].



We have recently reported the epoxy-epimination of cyclic 1,3-dienes by isomerization of the cycloadducts formed from such dienes with certain halonitrosoalkenes [6] [7]. This reaction merits particular attention since nitrosoalkenes are readily accessible, highly reactive intermediates which can be used *in situ*. In order to study the scope and limitations of this stereospecific reaction, which allows the functionalization of the four sp^2-centres of a diene in one step, it seemed interesting to vary the dienes and the substituents of the nitrosoalkene.

[1]) Taken in part from the Ph. D-Thesis of E. Francotte (1978), present address: *Ciba-Geigy AG*, Zentrale Forschung, CH-4002 Basel.

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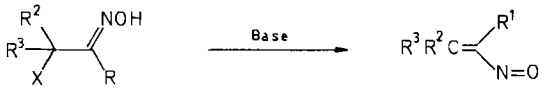
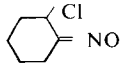
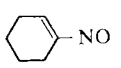
Synthesis of nitrosoalkenes. – The nitrosoalkenes reported were generally obtained by dehydrohalogenation of halooximes.



2 **1**

Table 1. *Spectroscopic characteristics of nitrosoalkenes* **1**

Oxime (**2**)	Ref.	Nitrosoalkene (**1**)	Ref.	^{1}H-NMR. ($CDCl_3$) δ ppm	IR. (CH_2Cl_2) cm^{-1}	UV./VIS. (CH_2Cl_2) λ(nm)	ε[g]
a $Cl_3C-C(=NOH)-H$	[14] [15]	$Cl_2C=CHNO$	[a]	6.74	1580, 1430	275 296 780	7000 6500 20
b $Cl_3C-C(=NOH)-Cl$	[15]	$Cl_2C=CClNO$	[a]	–	1610, 1460	320[h] 740	
c $Cl_3C-C(=NOH)-CH_3$	[a][b]	$Cl_2C=C(CH_3)NO$	[a]	1.43	1590, 1465	282 306 770	4000 5900 20
d $Br_3C-C(=NOH)-H$	[16]	$Br_2C=CHNO$	[a]	7.20	1660, 1430	795[h]	
e $Cl_2CH-C(=NOH)-Cl$	[a][c]	$ClHC=CClNO$	[a]	6.30	1525, 1480		
f $(H_3C)_3CCl_2C-C(=NOH)-H$	[a][d]	$(H_3C)_3CClC=CHNO$	[a][f]				
g $H_5C_6ClHC-C(=NOH)-Cl$	[a][c]	$H_5C_6HC=CClNO$	[a]		1600,1440	350[h] 703	
h $Cl_3C-C(=NOH)-NH_2$	[e]	$Cl_2C=C(NH_2)NO$	[a]	5.09	1620, 1420	405[h] 730	
i 	[5]		[5]	8.68	1630	255[i] 275 720	
j $((H_3C)_3C)_2ClC-C(=NOH)-H$	[10]	$((H_3C)_3C)_2C=CHNO$	[10]	6.30	1485	–	
k $ArClHC-C(=NOH)-CH_3$	[9]	$ArHC=C(CH_3)NO$	[9]	1.05–1.14 9.06–9.19	1600	732	46–56
l		$F_2C=CFNO$	[17]	–	1600	675	

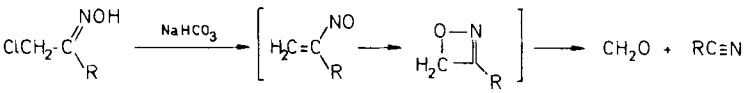
[a]) This work. [b]) Prepared by condensation of the 1.1.1-trichloro acetone with hydroxylamine (2 equiv.) in the presence of pyridine in ethanol (yield 80%). [c]) Obtained by treatment of the nitroalkene with $TiCl_4$ in CH_2Cl_2 at 0° [18]. [d]) Obtained by addition of NOCl in the presence of $AlCl_3$ on *t*-butylacetylene, followed by hydrolysis. [e]) Prepared by addition of hydroxylamine to trichloroacetonitrile [19]. [f]) Characterized only by his cycloadduct **7f**. [g]) Approximative values. [h]) In $CHCl_3$. [i]) In heptane.

This principle of 1,4-elimination using organic or inorganic bases has been long known and the transient appearance of nitrosoalkenes has sometimes been detected by the presence of a blue or green coloration [8]. Isolation of nitrosoalkenes, however, has only been achieved in a limited number of cases [5] [9] [10] *(Table 1)*.

We have prepared and characterized a series of halonitrosoalkenes **1a–h** by treatment of the α-polyhalooximes **2a–h** with $NaHCO_3$ or K_2CO_3 in dichloromethane *(Table 1)*. Only the nitrosoolefin **1c** could be isolated pure at room temperature whereas the others were stable in solution for a few weeks and could be kept for months at $-20°$. They were all characterized by an absorption between 630 and 800 nm in their visible spectra, values similar to those exhibited by nitrosoalkanes [11] [12] and corresponding to an $n \rightarrow \pi^*$ transition. The $\pi \rightarrow \pi^*$ transitions give two absorption bands in the UV. range ($\varepsilon = 4\text{–}7 \times 10^3$ for **1a** and **1c**). The absorption band of the nitroso group in the IR. is reported between 1500 and 1620 cm^{-1} [1] [11]. The IR. spectra of the nitrosoalkenes **1a–h** generally show two bands in this region, the absorption at 1580–1660 can be attributed to C=C stretching and that at 1420–1480 to N=O [13]. The lowering of the IR. frequency of the NO group can be explained by the effect of conjugation and of the halogen substitution in β-position.

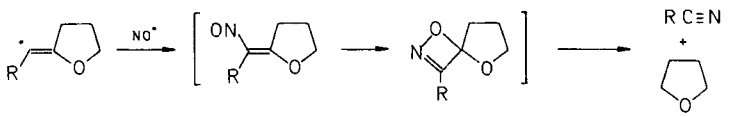
The ^{1}H-NMR. spectrum showing only NH_2 proton signals for the nitrosoenamine **1h** demonstrates the absence of any tautomeric nitrosoimine.

α-Monohalooximes also react in dichloromethane with inorganic bases ($NaHCO_3$, K_2CO_3) at room temperature by liberation of CO_2 but without appearance of coloration. Most of the transient nitrosoalkenes have been characterized by *in situ* cycloadditions *(vide infra)*. Their instability can be explained by the ready decomposition of an intermediate oxazete (**3**) produced by intramolecular cyclization.

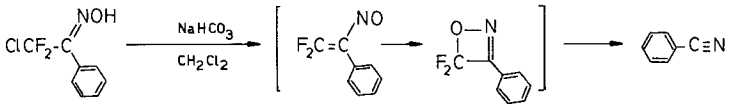


2 **1** **3**

This mechanism is supported by the fact that the corresponding oxazete is isolated by thermolysis of the 2,2′-di-*t*-butylnitrosoethylene (**1j**) [10]. Oxazetes have also been postulated as intermediates in certain reactions of vinyl radicals and NO·, implying the initial formation of nitrosoalkenes [20] and in oxidation of 1,1-bis(methylthio)-3,3-dimethyl-2-butanone oxime [21]. We observed this kind

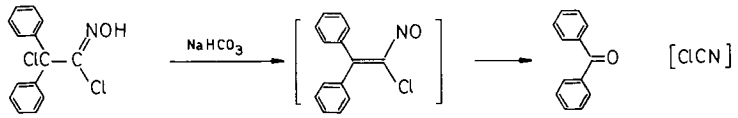


of degradation also with CF_2Cl as substituent. In fact, when the oxime of difluorochloroacetophenone **2m** is treated with $NaHCO_3$ in dichloromethane (even in the presence of cyclopentadiene), only benzonitrile is isolated. Analogously, only the



2m **1m**

formation of benzophenone can be observed from **2n** when it is treated with $NaHCO_3$ under the same conditions as **2m**.



2n **1n**

Reactivity of Nitrosoalkenes. – α,β-Unsaturated systems conjugated with electron-withdrawing groups have aroused great interest in organic synthesis. They react readily as '*Michael* acceptors' with nucleophiles and as dienes or dienophiles in cycloadditions. Until recently [6] [22], nitrosoalkenes have been neglected as members of this class.

Substitution. In numerous substitutions of α-monohalooximes with amines [8b,c] [23], thiols [8c] [24a], alcohols [8c,d] [24], enamines [25] and *Grignard* reagents [8b] [23b] nitrosoalkenes probably act as intermediates. Kinetic studies of certain of these reactions have proved an elimination-addition mechanism (*via* nitrosoalkenes) [8c,d] [23a]. We observed the facile substitution of halogen atoms of the trichloromethyl group of oximes **2a,c,d** by alkoxy groups [26] in the presence of a very weak base such as $NaHCO_3$, also explained by the intermediate formation of nitrosoalkenes. Repetition of the elimination-addition steps eventually leads to the production of the thermally unstable orthoesters **4** which yield oximinoesters **5**. The whole sequence is analogous to the formation and decomposition of α-orthonitroesters [27].

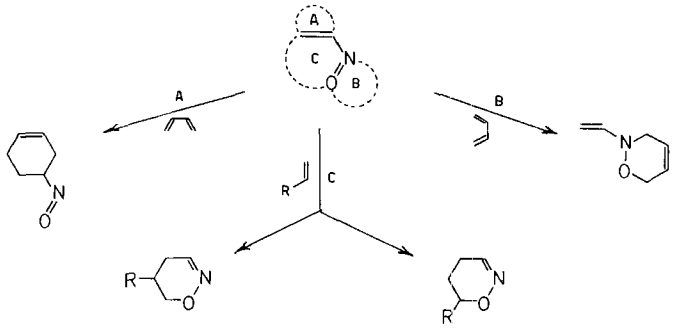
2a,c,d **1** **4** **5**

$R^2 = CH_3, C_2H_5$
R^1 = **a** and **d**: H, **c**: CH_3
X = **a** and **c**: Cl, **d**: Br

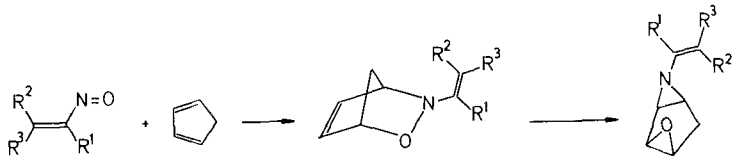
Cycloaddition. The dienophilic character of electron deficient nitroso compounds has long been known. Tertiary aliphatic nitroso compounds substituted by electron-withdrawing groups and most nitroso-aromatic compounds react rapidly with dienes to form moderately stable oxazine derivatives [2].

Similarly, nitrosoalkenes react with dienes either as dienophile (mode A or B) or diene (mode C), the selectivity depending on the substituents of the nitroso-

alkene. Although mode B is clearly observed, the question, if both the reaction A and C or only one of them takes place, remains open. In fact, the product formed by mode A, neither isolated nor characterized, might easily undergo a [3,3]-sigmatropic rearrangement to give one of the possible products formed directly by mode C.

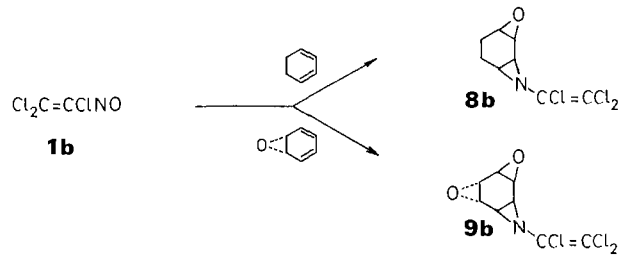


β-Substituted nitrosoalkenes behave quite differently towards dienes from the unsubstituted analogues at this position. The nitrosoalkenes **1a–g** (*β*-substituted), generated *in situ*, react with cyclopentadiene to form [4+2]-adducts at the N=O double bond and these adducts isomerize at RT. to form epoxyepimines. The latter process is analogous to the rearrangement of endoperoxides formed by the reaction of singlet oxygen with cyclodienes [28].



The adduct **6a** has been characterized by its low-temperature ^{1}H-NMR. spectrum [6a]. The structure of **7a** has been determined by X-ray analysis [6b] and that of the epoxyepimines **7b–g** follows from the similarity of their spectral characteristics to those of **7a** [6] *(Table 2)*.

Trichloronitrosoethylene **1b** reacts with both 1,3-cyclohexadiene and oxepin to form the corresponding epoxyepimines **8b** and **9b** *via* [4+2]-cycloaddition to the N=O double bond [7].



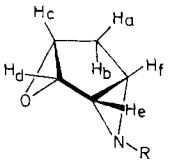
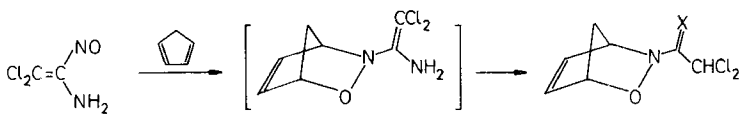


Table 2. *Yields and spectroscopic data of epoxyepimines* 7**a**–**g**

Epoxy-epimine 7	R	Yield %	M.p.	^{1}H-NMR. ($CDCl_3$) [δ ppm]					IR. (CH_2Cl_2) [ν. cm^{-1}]	Mass [m/z]
				H_a ($d \times m$)	H_b (d)	H_cH_d (br. s)	H_eH_f (m)	H of R		
a	$HC{=}CCl_2$	65	52–53°	1.73	2.18	3.70	2.95	6.33	2990, 1616, 1371	M^+ 191, 174, 162, 156, 127, 95, 93, 81, 66
b	$ClC{=}CCl_2$	45	64–65°	1.78	2.19	3.62	2.95	–	2990, 1595, 1370	M^+ 225, 190, 171, 156, 117, 104, 81
c	$(H_3C)C{=}CCl_2$	17	oil	1.68	2.11	3.57	2.93	1.88	2990, 1600, 1370	M^+ 205, 170, 151, 136, 97, 81
d	$HC{=}CBr_2$	40	100–102°	1.78	2.19	3.62	2.95	6.70	2960, 1340	M^+ 279, 250, 210, 183, 151, 120, 105, 93, 8
e	$ClC{=}CClH$	30	oil	1.78	2.19	3.73	2.96	6.17	2940, 1610, 1360	M^+ 191, 174, 156, 132, 119, 83
f	$HC{=}CClC(CH_3)_3$	40	oil	1.61	2.10	3.61	2.70	1.05 5.98	2960, 1365	M^+ 213, 198, 184, 159, 144, 108, 103, 81
g	$ClC{=}CHC_6H_5$	45	oil	1.68	2.13	3.60	3.00	6.10 6.95–7.4	2990, 1625, 1365	M^+ 233, 198, 179, 164, 125, 112

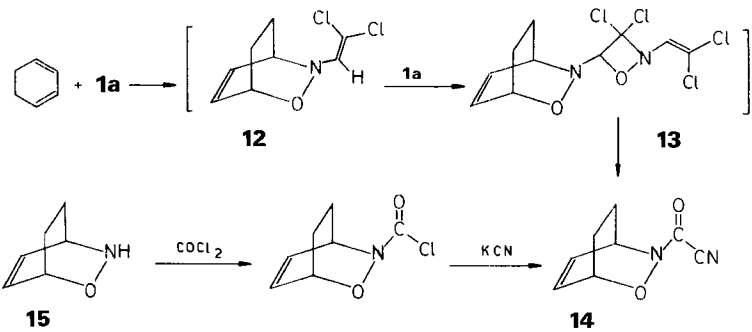
[a]) For fragments containing halogen atoms, only the lightest isotope peak is given.

In contrast, some adducts do not isomerize to epoxyepimines but undergo other transformations. The cycloadduct **10** of **1h** with cyclopentadiene, detected as the tautomeric compound **11a**, hydrolyzes readily to the amide **11b**.



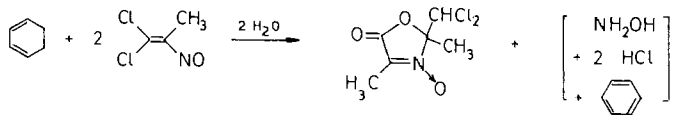
1h **10** **11a** X = NH **b** X = O

β-Dichloronitrosoethylene **1a** forms with 1,3-cyclohexadiene the α-ketonitrile **14** independently obtained by reaction of the bicyclic oxazine **15** with phosgene and then KCN [29]. The ketonitrile **14** probably arises from a reaction between the first adduct **12** and a second molecule of nitrosoalkene leading to the unstable intermediate **13** ([2+2]-cycloaddition); by loss of HCl and intramolecular fragmentation **13** would give **14**.



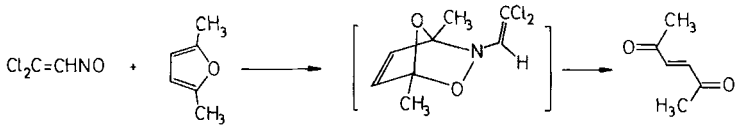
12 **13** **15** **14**

The nitrosoalkene **1c** also follows a different reaction path probably *via* an ene-reaction when treated with cyclohexadiene to form the oxazolidinone *N*-oxide **16** in low yield [30].



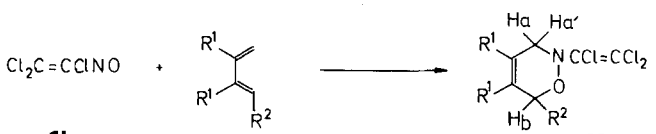
1c **16**

Compound **1a** generated in dichloromethane reacted with 2,5-dimethylfuran to give the hexenedione **18** [31] in 59% yield. The decomposition of the adduct **17**, assumed to be formed first, is probably similar to that known in the reaction of singlet oxygen with furan derivatives in aprotic medium [32]. An analogous reaction occurred with diphenyl isobenzofuran, giving the corresponding diketone in 75% yield.



1a **17** **18**

Compound **1b** reacted with substituted butadienes gave in good yields stable adducts with oxazine structures **19a–c**. Their spectroscopic characteristics *(Table 3)* are similar to those of this type of compound [2] [33]. We observed high regioselectivity in the case of **19c** where only one isomer was formed.

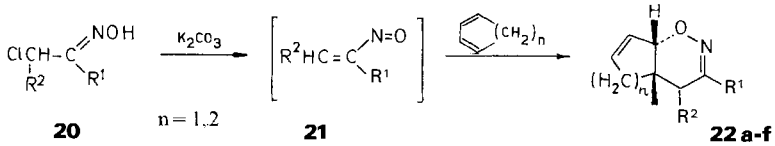


1b **19a-c**

Table 3. *Yield and ^{1}H-NMR. data (δ, ppm) of dihydrooxazine derivatives* **19a–c** ($CDCl_3$)

Oxazine	R^1	R^2	Yield %	R^1	R^2	$H_aH_{a'}$	H_b
19a	H	H	82	5.7	4.38	3.47	4.38
19b	CH_3	H	87	1.55, 1.62	4.17	3.3	4.17
19c	H	OCH_3	74	5.6–6.1	3.42	3.18, 3.75	4.92

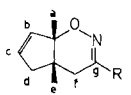
In order to investigate the factors responsible for isomerization of the appropriate adducts into epoxyepimines, we analyzed the behaviour of nitrosoalkenes **21a–d**, unsubstituted in β-position, with cyclodienes. These nitrosoalkenes are generated *in situ* from α-chloromethyloximes **20** by treatment with K_2CO_3. Reaction with cyclopentadiene or 1,3-cyclohexadiene gave adducts **22** different from epoxyepimines. The same type of product was obtained from compound **21e**. On the basis of ^{1}H- and ^{13}C-NMR. measurements, including selective decoupling and in agreement with independent studies [22], these adducts were shown to be oxazines **22a–f** *(Table 4)*.



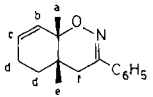
20 n = 1,2 **21** **22a-f**

Two mechanisms (mode A or C) have been discussed for the formation of these oxazines [22]. While the reaction of certain alkenes [22b] favours a regioselective [2+4]-addition (mode C) with the nitrosoalkene as the 4π-electron component, a [2+4]-addition (mode A) of the N=O bond on the diene, followed by [3+3]-sigmatropic rearrangement of the adduct cannot be excluded.

Table 4. *Yields and spectroscopic data of oxazines* **22a–f**



22a-e



22f

Oximes **20**	Oxazines **22**	R	Yield %	IR. (CH_2Cl_2) [$\tilde{\nu}$, cm^{-1}]	Mass [*m/z*]	^{1}H-NMR. ($CDCl_3$) [δ, ppm] R	H_a	H_b	H_c	H_{def}
$ClCH_2-C(=NOH)-CH_2Cl$	**a**	CH_2Cl	72	2910, 1610, 1425	M^+ 171, 154, 136, 118, 104, 96, 91, 78, 66	4.15 (*s*)	4.76 (*d*)	5.98 (*m*)	5.73 (*m*)	2.0–2.8 (*m*)
$ClCH_2-C(=NOH)-CH_3$	**b**	CH_3	23	2900, 1610, 1430	unstable oil	1.43 (*s*)	4.68 (*d*)	5.94 (*m*)	5.75 (*m*)	1.6–2.80 (*m*)
$ClCH_2-C(=NOH)-C_6H_5$ [35]	**c**	C_6H_5	87	2950, 1445	M^+ 199, 181, 117, 103	7.4–7.58 (*m*)	4.90 (*d*)	6.00 (*m*)	5.82 (*m*)	2.20–2.90 (*m*)
$ClCH_2-C(=NOH)-CN$ [36]	**d**	CN	40	2930, 2240	M^+ 148, 133, 106, 93, 81, 66	–	4.90 (*d*)	6.09 (*m*)	5.91 (*m*)	2.10–2.90 (*m*)
$Cl_2CH-C(=NOH)-H$	**e**	H	13	1600, 1430	unstable oil	7.63 (*s*)	5.22 (*d*)	5.93 (*m*)	5.70 (*m*)	1.65 (H_d) (*m*) 2.48 (H_e) (*m*) 3.38 (H_f) (*m*)
$ClCH_2-C(=NOH)-C_6H_5$ [35]	**f**	C_6H_5	48	2940, 1445	M^+ 213, 194, 117, 104, 103, 91, 79	7.03–7.67 (*m*)	4.07 (*t*)	5.8 (*m*)		1.38–2.90 (*m*)

^{13}C-NMR. spectral data of oxazines **22a,c** ($CDCl_3$) [δ, ppm]

	C_a	C_b	C_c	C_d	C_e	C_f	C_g	R			
22a	84.3	137.0	128.9	26.2	35.6	39.5	167.0	44.6			
22c	84.4	136.0	129.0	26.6	36.3	39.4	169.3	135.0	128.5 (*o*)	125.8 (*m*)	130.0 (*p*)

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Experimental Part

General procedure for the reaction of oximes with alcohols. A methanolic or ethanolic solution of the oximes **2a,c,d**, was stirred for 12 h in the presence of $NaHCO_3$. With methanol **2a** and **2d** give, after evaporation of the excess alcohol, the unstable orthoester $(H_3CO)_3C-CH=NOH$: – IR. (CH_2Cl): 3560, 1400 and 1105 cm^{-1}. – ^{1}H-NMR. ($CDCl_3$): 3.30 (*s*, 9 H); 7.22 (*s*, 1 H); 8.78 (br. OH). This orthoester can be prepared more conveniently by addition of a methanolic solution of **2a** to a solution of sodium methanolate. Under the same conditions **2a,d** and ethanol give $H_5C_2O-CO-CH=NOH$ while **2c** gives $H_5C_2O-CO-C(CH_3)=NOH$. These oxime esters have already been prepared [34].

General procedure for the reaction of nitrosoalkenes with dienes. Solutions of the oximes **2a–h** (0.01 mol) in CH_2Cl_2, $CHCl_3$ or acetonitrile (50 ml) were treated with a suspension of K_2CO_3 or $NaHCO_3$ at RT. in the presence of excess of 1.3 dienes for 1 to 20 h. After filtration and evaporation of the solvent, the remaining oil or solid was purified by column chromatography (SiO_2; cyclohexane/EtOAc 1:1) in the case of **7b**, **7c**, **11b**, **14**, **18**, **22b**, **22e** and **22f**. Compound **7a** was purified by recrystallization in ether and **22c** (m.p. 78–78.5°) in petroleum ether. The following compounds have been distilled: **19a** and **19c** at 65–70°/0.03 Torr; **22a** at 50°/0.04 Torr.

Data of **11b**. M.p. 55°. – IR. ($CHCl_3$): 2940, 1660, 1575, 1360 cm^{-1}. – ^{1}H-NMR. ($CDCl_3$): 6.5 (*m*, 2 H); 6.1 (*s*, 1 H); 5.4 (*m*, 2 H); 2.0 (*m*, 2 H). – MS.: $M^+ = 207$.

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