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The (apparently disrotatory) thermal ring opening of 4-nitro-1-cyclobuten-1-amines

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Abstract. A series of 4-nitro-1-cyclobuten-1-amines **3** was isolated from the thermal (2 + 2) cycloaddition of nitro(cyclo)alkenes **1** and ynamines **2**. Heating of **3a-d** yielded products corresponding with disrotatory ring opening *viz.* the 1,3-dienes **6a-d**. Heating of **3e,f** at 60 °C gave the dienes **7a,b**, as the result of a *conrotatory* ring opening reaction, together with the *trans*-2-nitrocyclobutenes **8a,b**, as the result of a hydrogen shift in the cyclobutene ring. Upon prolonged heating at 80 °C **8b** was converted into the diene **7b**. Treatment of **3e** with acid yielded the 2-nitrocyclobutenes **9a** and **9b**. The structures of **3a**, **3f**, **6a** and **7b** were elucidated by X-ray analysis. The formation of **6a-d** is attributed to *E*/*Z* isomerization of the product, initially formed by a conrotatory ring opening.

Introduction[1]

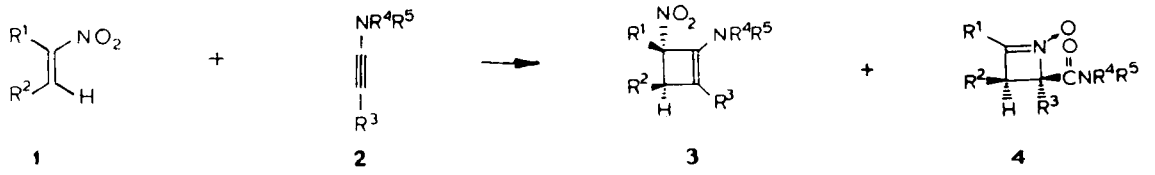
For a number of years we have been interested in the chemistry of cyclobutenes, particularly in their synthesis by a thermal (2 + 2) cycloaddition of enamines of cyclic ketones with electron-deficient alkynes[2-5]. The subsequent thermal isomerization of the (2 + 2) cycloadducts represents a convenient method for the preparation of medium- and large-sized rings[6-10]. This ring opening of substituted (hetera)-cyclobutenes has been the subject of many theoretical and synthetic studies[11-16]. The stereochemistry of these valence isomerization reactions is usually that expected from conservation of orbital symmetry. However, examples that seemed to contradict the *Woodward–Hoffmann* rules have been reported[17-19]. In particular, cyclobutenes with strongly polarizing substituents give rise to deviations from the *normal* ring opening reaction. Polar groups may have a large influence on the ring opening, because their empty or occupied *p* orbitals can mix with the HOMO or the LUMO of the cyclobutene, respectively[16,20]. Cyclobutenes fused with 5- or 6-membered rings seemed to open thermally in a disrotatory mode. In these cases steric factors might be the cause of the observed disrotatory ring opening[21]. However, we have recently reported that *N,N*-dialkyl-2-cyclobuten--1-amines rearrange thermally via a *conrotatory* electrocyclic pathway and that the resulting *N,N*-dialkyl-1,3-cycloalkadienamines may subsequently undergo (rapid) isomerization to give stable compounds that were previously interpreted as the initial disrotatory ring opening products[22]. Our results have clarified a number of apparent deviations[17,19] from the generally observed conrotatory mode of ring opening.

In our study on the thermal ring opening of *heteracyclobutenes*, *viz.* *N*-hydroxy-1,2-dihydroazetes, prepared *in situ* by treatment of four-membered cyclic nitrones with base, we observed a strong preference for outward rotation of the hydroxyl group. The formation of the apparently disrotatory ring opening products was explained by *N* inversion in the *N*-hydroxyazetine anion prior to the ring-opening reaction[23,24].

Our continuing interest in the effect of strongly polarizing substituents on electrocyclic reactions and the theoretical work of *Epiotis*[13] that predicts the lowering of the activation energy of a thermally "forbidden" disrotatory ring opening of cyclobutenes when such substituents are present at the termini of the π-system, has led us to investigate the stereochemistry of the ring opening of cyclobutenes that have a strongly *electron-withdrawing* nitro substituent at one of the sp^3-hybridized carbon atoms. *Miller* et al.[25] found that the thermal ring opening of *cis*-1,3-dinitro-2,4-diphenylcyclobutene yielded the *disrotatory* ring opening product, *viz.* (*Z,E*)-1,3-dinitro-2,4-diphenylbutadiene. They explained the formation of this disrotatory ring opening by assuming a conrotatory ring opening, followed by *E*/*Z* isomerization. Under their reaction conditions all other 1,3-dinitrocyclobutenes examined, did ring open in a conrotatory fashion. In this paper the synthesis of *N,N*-dialkyl-4-nitro-1-cyclobuten-1-amines **3** by a (2 + 2) cycloaddition of electron-deficient nitroalkenes **1** and electron-rich ynamines **2** and the thermal isomerization of these compounds are described.

Results

Previously we have reported that reaction of the nitroalkenes **1** with ynamines **2** yields mixtures of *N,N*-dialkyl--4-nitro-1-cyclobuten-1-amines **3** and four-membered cyclic nitrones **4** (Scheme 1)[26]. These products can be regarded as being derived from a (2 + 2) and a (4 + 2) cycloaddition,



1 **2** **3** **4**

	R^1	R^2			R^3	NR^4R^5
1a	H	Ph	(E)	**2a**	Ph	$N(Me)_2$
1b	D	Ph	(E)	**2b**	Ph	$N(CH^2)^4$
1c	Me	Ph	(E)	**2c**	Ph	$N(Et)_2$
1d	Ph	Ph	(E)	**2d**	Ph	$N(CH_2CH_2)_2O$
1e	$---(CH_2)_3---$			**2e**	Me	$N(Et)_2$
1f	$---(CH_2)_4---$			**2f**	Me	N(Me)Ph
1g	$---(CH_2)_6---$					
1h	Br	Ph	(Z)			
1i	Me	3-Br-C_6H_4	(E)			
1j	Me	2-OMe-C_6H_4	(E)			
1k	Me	3,4-OCH_2O-C_6H_3	(E)			

	R^1	R^2	R^3	NR^4R^5
3a	Me	Ph	Ph	$N(Me)_2$
3b	Me	Ph	Ph	$N(CH_2)_4$
3c	Me	Ph	Ph	$N(Et)_2$
3d	Me	Ph	Ph	$N(CH_2CH_2)_2O$
3e	H	Ph	Ph	$N(CH_2)_4$
3f	H	Ph	Ph	$N(CH_2CH_2)_2O$
3g	D	Ph	Ph	$N(CH_2CH_2)_2O$
3h	$-----(CH_2)_3----$		Ph	$N(Me)_2$
3i	$-----(CH_2)_4----$		Ph	$N(Me)_2$
3j	$-----(CH_2)_6----$		Ph	$N(Me)_2$
3k	Br	Ph	Ph	$N(Me)_2$
3m	Me	3-Br-C_6H_4	Me	$N(Et)_2$
3n	Me	2-OMe-C_6H_4	Me	$N(Et)_2$
3p	Me	3,4-OCH_2O-C_6H_3	Me	$N(Et)_2$
3q	Me	Ph	Me	N(Me)Ph

Scheme 1

respectively. Since initially we were mainly interested in the chemistry of the four-membered cyclic nitrones as novel synthons in heterocyclic chemistry[27,28] and because the (2 + 2) cycloadducts were difficult to isolate, we have only recently concentrated our efforts on the synthesis and isolation of the 4-nitro-1-cyclobuten-1-amines **3** in order to study thermal isomerization reactions.

Preparation of the starting materials

The syntheses of the nitroalkenes **1** and of the ynamines **2**, with the exception of the nitroalkenes (*E*)-[2-($^2H_1$)-2-nitroethenyl]benzene (**1b**) and (*Z*)-(2-bromo-2-nitroethenyl)-benzene (**1h**) have been described in detail[29]. Condensation of benzaldehyde and nitromethane-d_3, with sodium hydroxide-*d* yielded the nitroalkene **1b**[30]. Compound **1h** was prepared by the addition of bromine to the nitroalkene **1a**, followed by elimination of hydrogen bromide upon treatment of the dibromide with pyridine[31].

Reaction of nitro(cyclo)alkenes **1** *and ynamines* **2**[32]

When the reactions of nitro(cyclo)alkenes **1** and ynamines **2** were performed in apolar solvents like petroleum ether or tetrachloromethane, the reaction mixture was stirred at room temperature for 16 h. When a polar solvent (acetonitrile) was used, the reaction mixture was stirred for 1 h at 0 °C and for an additional 3–5 h at room temperature. After the reaction was complete the reaction mixture was concentrated under reduced pressure. The four-membered cyclic nitrones **4** either crystallized spontaneously, or solidified upon addition of diisopropyl ether. Further trituration of the solid with diisopropyl ether yielded the pure four-membered cyclic nitrones[29]. The concentrated filtrate was submitted to column chromatography (Al_2O_3, petroleum ether/diethyl ether mixtures). Collection of the fast eluting fractions ($R_f \approx 0.8$–0.95) gave the pure *N,N*-dialkyl-4-nitro-1-cyclobuten-1-amines **3**[33], which were isolated as crystalline, orange colored compounds (**3a**, **3b**, **3e-h** and **3k**) or as orange oils (**3c**, **3d**, **3i**, **3j** and **3m-q**) in yields of 12–75%.

Characterization of the (2 + 2) cycloadducts

The structural and spectral data of the *N,N*-dialkyl-4-nitro-1-cyclobuten-1-amines **3** show some general features (Table I). The absorptions of the nitro group are present at ~1540 and ~1345 cm^{-1} in the infrared spectra. In the ^{13}C NMR spectra the effect of the dialkylamino function on the chemical shifts of both C-1 and C-2 is obvious. The C-1 carbon atoms absorb at δ 138.4–143.0 and C-2, depending on both the amine function and the substituent R^3 absorbs at δ 104.6–120.8. C-3 is present as a doublet at δ 44.5–56.9, whereas C-4, bearing the nitro group, absorbs at lower field, δ 88.1–97.3. The ^1H NMR data point to a stereochemistry of **3** with a *cis* relationship between the groups R^1 and R^2. In compounds **3e,f** a small *trans* coupling constant of 1.2 Hz is found for H-3 and H-4 consistent with R^1 and R^2 being *cis*[34]. The absorption in the ^1H NMR spectra of the methyl groups at C-4 of **3a-d** and **3m-q** between δ 1.25 and δ 1.37 also clearly shows a *cis* relationship between the methyl group (R^1) and the aryl group (R^2), since a methyl group which is not shielded by an aromatic nucleus would give rise to an absorption at much lower field as for instance is found for R^3 in the four-membered cyclic nitrones[26].
The protons at C-3 show absorptions between δ 3.70 and δ 4.46. It is obvious that this difference in chemical shift is caused by the presence of substituents in the phenyl moiety (R^2), because C3–H in the compounds **3m-q** is present at δ 3.70–4.24. X-ray analysis of compounds **3a** and **3f** revealed definitively a *cis* relationship between R^1 and R^2 (Figs. 1 and 2)[35]. In the compounds **3h-k**, no specific spectroscopic probes are present, but the analogy of the NMR data with those of compounds **3d** and **3m-q** indicate that these 4-nitro-1-cyclobuten-1-amines have the same stereochemistry, *i.e.* a *cis* relationship of the groups R^1 and R^2.
From the X-ray data of the 1-cyclobuten-1-amines **3a** and **3f** and of the previously reported dimethyl 8-(1-piperidinyl)-bicyclo[5.2.0]non-8-ene-1,9-dicarboxylate (**5**)[22] some general remarks can be made on the structure of the cyclobutene ring (Tables II and III). The torsion angles for the cyclobutene rings around the double bond [*i.e.*

Table I Spectral data of the N,N-*dialkyl-4-nitro-1-cyclobuten-1-amines* **3**.

Comp.	^{1}H NMR[a] (toluene-d_8) δ			^{13}C NMR[a] (toluene-d_8) δ				MS *(m/z)*		IR (KBr) ν (cm^{-1})	
	H-3	R^1 (s)	R^3	C-1 (s)	C-2 (s)	C-3 (d)	C-4 (s)	(Calcd.) exp.	Formula	C=C	NO_2
3a	4.36 (s)	1.27	[b]	143.0	111.4	53.8	90.5	(308.153) 308.149	$C_{19}H_{20}N_2O_2$	1660 1535	1350
3c	4.46 (s)	1.37	[b]	141.6	110.8	53.8	91.0	(336.184) 336.182	$C_{21}H_{24}N_2O_2$	1650 1530	1340
3d	4.37 (d)	1.27	[b]	142.0	115.7	53.8	90.7	(350.163) 350.162	$C_{21}H_{22}N_2O_2$	1650 1530	1320
3f	4.33 (d)[c]	5.15 (d)[c]	[b]	139.3	115.7	48.7	86.0 (d)	(336.147) 336.149	$C_{20}H_{20}N_2O_3$	1655 1550	1350
3g	4.34	–		139.4	116.2	48.8	–	(337.154) 337.146	$C_{20}H_{19}DN_2O_3$	1650 1530	
3h	3.33 (m)	[d]	[b]	138.4	109.1	51.2	93.8	(258.137) 258.136	$C_{15}H_{18}N_2O_2$	1640 1530	1350
3i	3.19 (t)	[d]	[b]	141.4	112.9	44.5	88.1	(272.153) 272.151	$C_{16}H_{20}N_2O_2$	1655 1530	1330
3j	[d]	[d]	[b]	141.8	118.0	47.2	97.3	(300.184) 300.186	$C_{18}H_{24}N_2O_2$	1650 1530	
3k	4.48 (s)	–	[b]	140.1	112.4	56.9	93.1	(372.047) 372.044	$C_{18}H_{17}BrN_2O_2$	1655 1550	1330
3m	3.80 (q)	1.30	1.82 (d)[e]	141.7	104.6	55.3	90.6	(352.079) 352.079	$C_{18}H_{17}BrN_2O_2$	1620 1550	1380
3n	4.24 (q)	1.25	1.92 (d)[e]	141.9	105.7	49.5	90.7	(304.179) 304.180	$C_{17}H_{24}N_2O_3$	1620	1380
3p	3.70 (q)	1.32	1.81 (d)[e]	141.8	105.1	56.0	90.8	(318.176) 318.163	$C_{17}H_{22}N_2O_4$	1680 1530	1380
3q	4.00 (q)	1.33	1.51 (d)[f]	140.4	120.8	56.1	92.3	(308.153) 308.153	$C_{20}H_{19}N_2O_2$	–	–

[a] **3f**, **3n-3q** (^{1}H NMR), and **3n,m** (^{13}C NMR) were recorded in $CDCl_3$. [b] Phenyl absorptions. [c] J_{trans} 1.2 ± 0.1 Hz. [d] Methylene absorptions. [e] J 1.0 ± 0.1 Hz. [f] J 1.2 ± 0.1 Hz.

C(sp^3)–C(N)=C(C)–C(sp^3)] are 6.2°, 4.1° and –3.0° for the compounds **3a**, **3f** and **5**, respectively, which indicates a nearly flat cyclobutene ring.

Although the stereochemistry of **3** is that expected if the (2 + 2) cycloadditions of nitroalkenes **1** and ynamines **2** proceed concertedly, this does *not* prove concertedness. The stereochemistry in the starting nitroalkenes is preserved in the cyclobutene, but this *trans* stereochemistry of the (2 + 2) cycloadducts (**3a** and **3f**) corresponds to the thermodynamically most stable configuration.

Thermal ring isomerization of the N,N-*dialkyl-4-nitro-1-cyclobuten-1-amines* **3**

Thermal ring opening of *trans-N,N*,4-trimethyl-4-nitro-2,3-diphenyl-1-cyclobuten-1-amine (**3a**) in benzene or toluene solution yielded (*Z,Z*)-*N,N*-dimethyl-4-nitro-1,2-diphenyl-1,3-pentadien-3-amine (**6a**) as established by X-ray analysis (Fig. 3;Table VII). Surprisingly this is the product in which the nitro group and the dimethylamino moiety are in a *cis* position. Therefore, compound **6a** is an apparent result of a *disrotatory* cyclobutene ring opening reaction *(vide infra)*.

The thermal ring opening of **3a-d** to yield the dienes **6a-d** was monitored by ^{1}H NMR spectroscopy (Scheme 2). The cyclobutene proton at C-3, and the methyl group at C-4 were used as probes (Table IV).

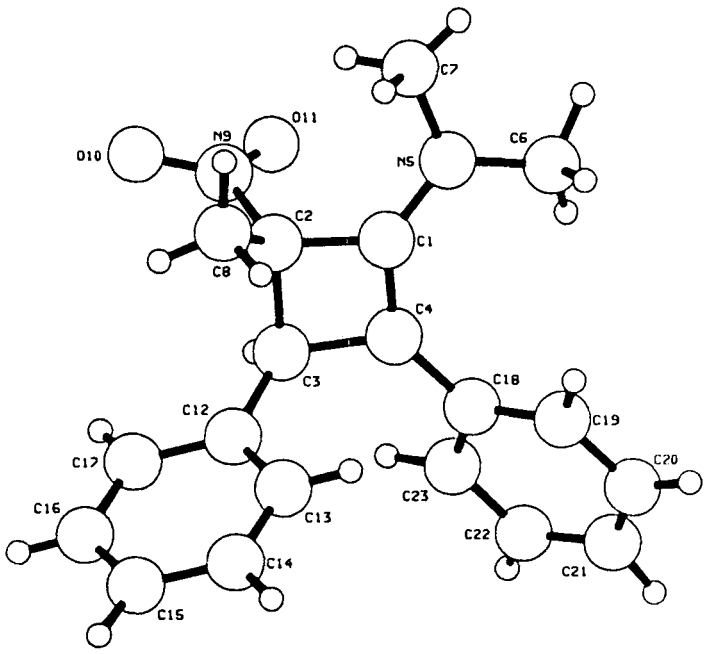


Fig. 1. Structure of **3a**.

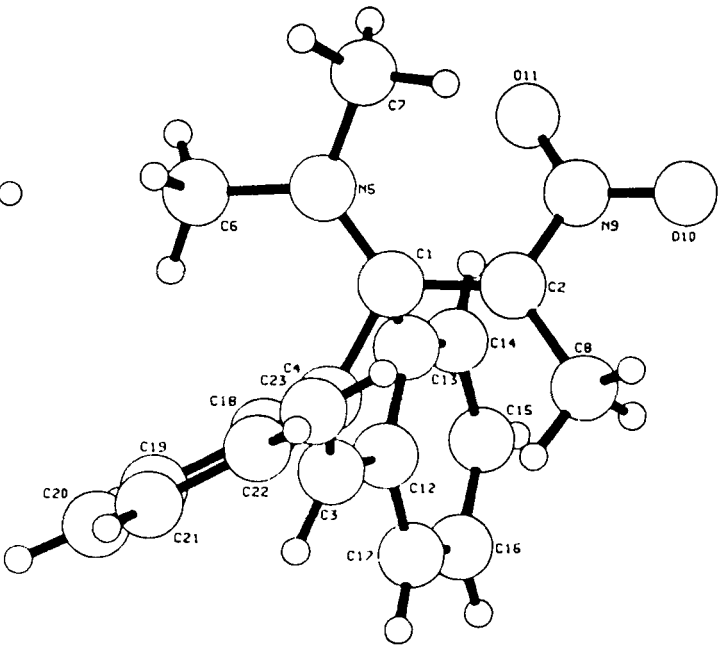


Fig. 3. Structure of **6a**.

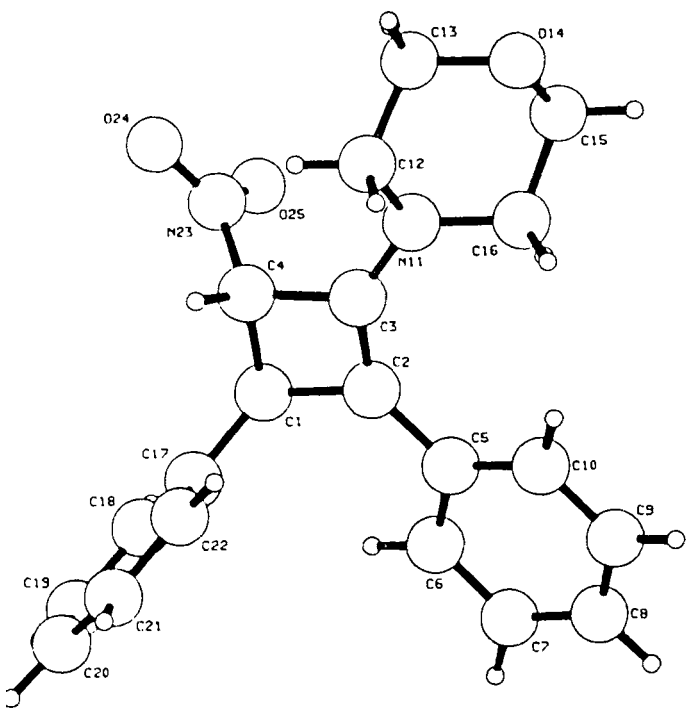


Fig. 2. Structure of **3f**.

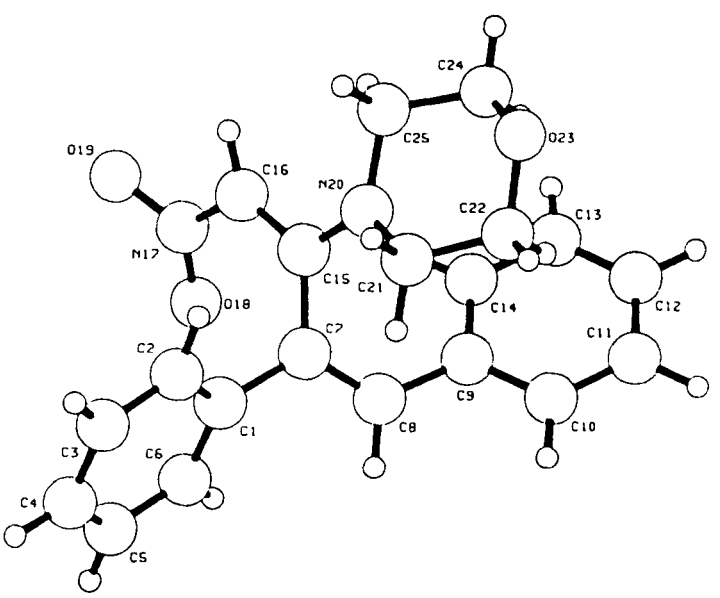
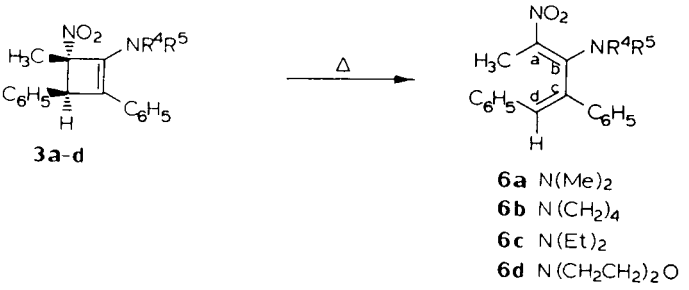


Fig. 4. Structure of **7b**.

Table II Positional parameters and their estimated standard deviations of compound **3a**.

Atom	x	y	z
O10	0.4598(1)	0.3918(3)	0.8507(2)
O11	0.5019(1)	0.2892(2)	1.0067(2)
N5	0.6648(1)	0.0773(2)	1.0010(2)
N9	0.5193(1)	0.3302(2)	0.9245(2)
C1	0.6817(1)	0.2114(2)	1.0025(1)
C2	0.6230(1)	0.3149(2)	0.9197(2)
C3	0.6910(1)	0.4223(2)	1.0021(2)
C4	0.7448(1)	0.3026(2)	1.0697(1)
C6	0.7205(2)	−0.0071(2)	1.0930(2)
C7	0.5907(2)	0.0150(2)	0.9077(2)
C8	0.6197(2)	0.3134(2)	0.7965(2)
C12	0.7447(1)	0.5186(2)	0.9495(2)
C13	0.8349(1)	0.4882(2)	0.9386(2)
C14	0.8806(1)	0.5765(2)	0.8863(2)
C15	0.8358(2)	0.6953(2)	0.8423(2)
C16	0.7465(2)	0.7263(2)	0.8513(2)
C17	0.7012(2)	0.6394(2)	0.9054(2)
C18	0.8298(1)	0.3054(2)	1.1744(2)
C19	0.9063(2)	0.2138(3)	1.2004(2)
C20	0.9843(2)	0.2231(3)	1.3034(2)
C21	0.9865(2)	0.3241(3)	1.3786(2)
C22	0.9136(3)	0.4160(3)	1.3531(3)
C23	0.8356(2)	0.4086(3)	1.2516(2)
H3	0.654(1)	0.474(2)	1.041(1)
H13	0.865(1)	0.406(2)	0.967(2)
H14	0.944(2)	0.556(2)	0.881(2)
H15	0.867(2)	0.754(3)	0.796(2)
H16	0.719(2)	0.806(2)	0.821(2)
H17	0.64412)	0.661(2)	0.915(2)
H19	0.905(1)	0.145(2)	1.144(2)
H20	1.026(2)	0.151(2)	1.311(2)
H21	1.038(2)	0.341(3)	1.451(2)
H23	0.778(2)	0.475(3)	1.234(2)
H22	0.910(2)	0.487(3)	1.407(2)
H6A	0.685(2)	−0.094(3)	1.098(3)
H6B	0.746(2)	0.042(3)	1.165(2)
H6C	0.770(2)	−0.048(4)	1.071(3)
H8A	0.578(2)	0.240(3)	0.750(2)
H8B	0.686(2)	0.298(2)	0.798(2)
H8C	0.603(2)	0.399(2)	0.766(2)
H7A	0.586(2)	−0.076(2)	0.917(2)
H7B	0.543(2)	0.069(2)	0.868(2)
H7C	0.615(2)	0.032(3)	0.840(3)



Scheme 2

Table IV Approximate half-lifes[38] *of the 4-nitro-1-cyclobuten-1--amines* **3a-3d** *in benzene-*d_6*-at 353 K.*

Comp.	$t\frac{1}{2}$
3a	18 min
3b	58 min
3c	74 min
3d	27 min

In the ^{1}H NMR spectra of the 1,3-dienes **6a-d** the methyl groups are present at δ 1.97–2.09 (Table V), which agrees well with the value of δ 2.04–2.07 found in *N*-alkyl-2-nitro--1-propen-1-amines, also having a *trans* relationship between the amino moiety and the methyl group[36,37].

The thermal ring opening of **3e** and **3f** with R^1 = H was also monitored by ^{1}H NMR spectroscopy (Scheme 3). After 1 h in benzene-d_6 at 60 °C the cyclobutene ring proton signals of **3f** at δ 4.33 and δ 5.15 (J_{trans} 1.2 Hz) had disappeared. Simultaneously two vinylic proton signals at δ 7.08 and 6.92, and two signals at δ 3.97 and 3.45 (J 1.5 Hz) had appeared (Tables V and VI). Two reaction products were formed which were separated by column chromatography. Both compounds were isomers of **3f** as established by mass spectrometry. The ^{13}C NMR spectrum of the first compound shows a singlet at δ 158.9, corresponding to an α-enamine carbon atom *(vide supra)*, whereas the doublet at δ 116.0 points to the presence of a nitro group at a C=CH moiety[39,40].

Table III Positional parameters and their estimated standard deviations of compound **3f**.

Atom	x	y	z	Atom	x	y	z
O14	0.3348	0.0994(2)	0.1050	C21	0.6358(1)	0.6276(3)	0.7339(3)
O24	0.6200(1)	0.0541(2)	0.4118(2)	C22	0.5908(1)	0.5152(3)	0.6655(2)
O25	0.5597(1)	−0.0468(2)	0.5317(2)	H1	0.555(1)	0.155(3)	0.696(2)
N11	0.4221(1)	0.1892(2)	0.3481(2)	H4	0.580(1)	0.289(3)	0.475(2)
N23	0.5789(1)	0.0628(2)	0.4819(2)	H6	0.477(1)	0.293(3)	0.834(2)
C1	0.5459(1)	0.2456(3)	0.6457(2)	H7	0.391(2)	0.384(3)	0.942(3)
C2	0.4624(1)	0.2710(2)	0.5837(2)	H8	0.267(2)	0.437(3)	0.826(3)
C3	0.4668(1)	0.2280(2)	0.4650(2)	H9	0.234(1)	0.441(3)	0.602(2)
C4	0.5503(1)	0.2150(3)	0.5049(2)	H10	0.319(1)	0.367(3)	0.494(2)
C5	0.4067(1)	0.3199(2)	0.6481(2)	H12A	0.497(1)	0.233(3)	0.252(2)
C6	0.4265(1)	0.3269(3)	0.7831(2)	H12B	0.429(1)	0.336(3)	0.206(2)
C7	0.3748(2)	0.3718(3)	0.8476(2)	H13A	0.436(1)	0.010(4)	0.160(3)
C8	0.3035(1)	0.4093(3)	0.7809(2)	H13B	0.422(1)	0.138(2)	0.047(2)
C9	0.2833(1)	0.4060(3)	0.6482(3)	H15A	0.343(1)	−0.047(3)	0.250(2)
C10	0.3345(1)	0.3635(3)	0.5827(2)	H15B	0.260(2)	0.047(3)	0.197(3)
C12	0.4442(1)	0.2266(3)	0.2314(2)	H16A	0.334(1)	0.130(3)	0.410(2)
C13	0.4137(1)	0.1107(3)	0.1304(2)	H16B	0.316(1)	0.274(3)	0.301(2)
C15	0.3150(1)	0.0561(3)	0.2188(2)	H18	0.641(1)	0.249(3)	0.872(2)
C16	0.3425(1)	0.1671(3)	0.3261(2)	H19	0.718(1)	0.432(3)	0.995(2)
C17	0.5930(1)	0.3713(3)	0.7168(2)	H20	0.717(2)	0.679(3)	0.899(3)
C18	0.6404(1)	0.3441(3)	0.8388(2)	H21	0.634(1)	0.726(3)	0.697(2)
C19	0.6845(1)	0.4573(3)	0.9069(2)	H22	0.559(1)	0.535(3)	0.578(2)
C20	0.6827(1)	0.5988(3)	0.8547(3)				

Table V Spectral data of the 1,3-dienes **6** *and* **7**.

Comp.	^{1}H NMR (toluene-d_8) δ			^{13}C NMR (toluene-d_8) δ					MS (*m/z*)	
	H-d (s)	NR^4R^5	CH_3 (s)	C-a (s)	C-b (s)	C-c (s)	C-d	CH_3 (q)	(Calcd.) exp.	Formula
6a	6.87	2.41 (s)	2.05	138.8	155.2	120.5	126.3 (s)	17.5	(308.153) 308.150	$C_{19}H_{20}N_2O_2$
6b	6.86	[a]	2.14	138.1	151.8	119.9	125.9 (s)	17.3	(334.168) 334.170	$C_{21}C_{22}N_2O_2$
6c	6.86	[b]	2.09	139.6	154.9	121.3	126.7 (s)	17.7	(336.184) 336.185	$C_{21}H_{24}N_2O_2$
6d	6.84	3.3–2.5 (m)	1.97	138.9	155.5	120.7	126.6 (s)	17.4	(350.163) 350.160	$C_{21}H_{22}N_2O_3$
7a	6.88	[c]	[d]	113.8 (d)	157.0	135.2	125.7 (d)	–	(320.153) 320.155	$C_{20}H_{20}N_2O_2$
7b	6.92	3.29 (br s)	[e]	116.0 (d)	158.9	134.0	125.9 (d)	–	(336.147) 336.145	$C_{20}H_{20}N_2O_3$

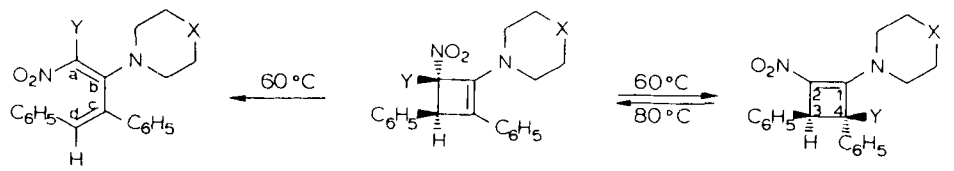
[a] 3.2–2.6 (m, 4H, NCH_2), 1.4–0.9 (m, 4H, CH_2). [b] 2.92 (q, 4H, NCH_2), 0.64 (t, 6H, $NCCH_3$). [c] 3.6–3.0 (m, 4H, NCH_2), 2.2–1.5 (m, 4H, CH_2). [d] 7.06 (s, 1H, H-a). [e] 7.08 (s, 1H, H-a).

Table VI Spectral data of the N,N-*dialkyl-2-nitro-1-cyclobuten-1-amines* **8** *and* **9**.

Comp.	^{1}H NMR ($CDCl_3$) δ		^{13}C NMR[a] ($CDCl_3$) δ				MS (*m/z*)	
	H-3	H-4 (d) $J_{3,4}$ (Hz)	C-1 (s)	C-2 (s)	C-3 (d)	C-4	(Calc.) exp.	Formula
trans-**8a**	4.02 (d)	3.43 1.5	151.3	110.6	53.6	53.8 (d)	(320.153) 320.152	$C_{20}H_{20}N_2O_2$
trans-**8b**	3.97 (d)	3.45 1.5	150.4	111.0	52.7	53.2 (d)	(336.147) 336.145	$C_{20}H_{20}N_2O_3$
cis-**9a**	4.82 (d)	4.22 5.7	151.2	110.2	49.4	49.5 (d)	(320.153) 320.153	$C_{20}H_{20}N_2O_2$
cis-**9b**	4.75 (d)	4.22 5.8	150.9	110.6	50.4	50.5 (d)	(336.147) 336.147	$C_{20}H_{20}N_2O_3$
cis-**9c**	4.81 (s)	– –	150.8	110.3	49.2	49.3 (t)[b]	(321.159) 321.157	$C_{20}H_{19}DN_2O_2$

[a] **8b** was recorded in toluene-d_8, and **9a** in a 1:1 mixture of $CDCl_3$ and acetone-d_6; internal standard TMS (0.00 ppm). [b] J_{CD} 6.3 Hz.

X-Ray analysis confirmed the butadiene structure of **7b** (Fig. 4; Table VIII), the result of a *conrotatory* ring opening reaction. The X-ray data of **6a** might point to a *diminished* degree of conjugation[41] between the dialkylamino and the nitro moiety as compared to **7b**. This can be tentatively concluded from the overall lengthening of the C=C and the C–NO_2 bonds in the nitroenamine system in **6a**. In **6a** the R^4R^5N–C=C–NO_2 bond lengths are 0.1340 nm,



7a X = –, Y = H
7b X = O, Y = H
7c X = O, Y = D

3e X = –; Y = H
3f X = O; Y = H
3g X = O; Y = D

8a X = –, Y = H
8b X = O, Y = H
8c X = O, Y = D

Scheme 3

Table VII Positional parameters and their estimated standard deviations of compound **6a**.

Atom	x	y	z
O10	0.1817(3)	0.0645(2)	0.3237(1)
O11	0.3728(3)	-0.0623(2)	0.3266(1)
N5	0.7005(2)	-0.0196(1)	0.2471(1)
N9	0.3195(3)	0.0197(2)	0.2979(1)
C1	0.5660(3)	0.0202(2)	0.2043(1)
C2	0.4028(3)	0.0601(2)	0.2319(1)
C3	0.5053(3)	-0.0245(2)	0.0677(1)
C4	0.6034(3)	0.0279(2)	0.1200(1)
C6	0.8473(4)	-0.0803(2)	0.2122(2)
C7	0.7200(4)	-0.0031(2)	0.3297(1)
C8	0.2955(4)	0.1389(2)	0.1900(2)
C12	0.3600(3)	-0.1002(2)	0.0788(1)
C13	0.3399(4)	-0.1599(2)	0.1449(1)
C14	0.2018(4)	-0.2305(2)	0.1497(1)
C15	0.0832(4)	-0.2452(2)	0.0897(2)
C16	0.1027(4)	-0.1882(2)	0.0241(1)
C17	0.2396(3)	-0.1166(2)	0.0185(1)
C18	0.7501(3)	0.0988(2)	0.0956(1)
C19	0.8686(3)	0.0741(2)	0.0358(1)
C20	0.9980(3)	0.1423(2)	0.0103(1)
C21	1.0124(3)	0.2365(2)	0.0441(1)
C22	0.8973(3)	0.2623(2)	0.1038(1)
C23	0.7686(3)	0.1940(2)	0.1298(1)
H3	0.527(2)	-0.007(1)	0.012(1)
H6A	0.959(5)	-0.041(3)	0.219(2)
H6B	0.859(5)	-0.140(2)	0.238(1)
H6C	0.818(5)	-0.105(2)	0.155(2)
H7A	0.635(3)	0.058(2)	0.346(1)
H7B	0.851(3)	0.008(2)	0.340(1)
H7C	0.686(3)	-0.066(2)	0.355(1)
H8A	0.357(5)	0.165(2)	0.139(2)
H8B	0.177(4)	0.114(2)	0.178(1)
H8C	0.284(6)	0.199(3)	0.217(2)
H13	0.427(3)	-0.150(2)	0.188(1)
H14	0.186(3)	-0.271(2)	0.196(1)
H15	-0.012(3)	-0.292(2)	0.093(1)
H16	0.020(3)	-0.201(2)	-0.016(1)
H17	0.250(3)	-0.077(2)	-0.027(1)
H19	0.862(3)	0.013(1)	0.013(1)
H20	1.087(4)	0.127(2)	-0.029(1)
H21	1.107(3)	0.285(2)	0.027(1)
H22	0.905(3)	0.328(2)	0.131(1)
H23	0.695(3)	0.210(1)	0.169(1)

Table VIII Positional parameters and their estimated standard deviations of compound **7b**.

Atom	x	y	z
O18	0.2153(2)	-0.0263(1)	0.1192(2)
O19	0.1316(3)	-0.0951(1)	0.0282(2)
O23	0.0953(1)	0.22847(9)	-0.2591(2)
N17	0.1599(2)	-0.0371(1)	0.0443(2)
N20	0.1143(1)	0.1273(1)	-0.0838(2)
C1	0.1193(2)	0.0907(1)	0.2185(2)
C2	0.0311(2)	0.0952(1)	0.2133(2)
C3	-0.0170(2)	0.0864(2)	0.3150(3)
C4	0.0214(2)	0.0723(2)	0.4214(3)
C5	0.1082(2)	0.0653(1)	0.4260(2)
C6	0.1570(2)	0.0745(1)	0.3261(2)
C7	0.1714(2)	0.1062(1)	0.1122(2)
C8	0.2408(2)	0.1447(1)	0.1191(2)
C9	0.2960(2)	0.1654(1)	0.0209(2)
C10	0.3258(2)	0.2314(1)	0.0158(2)
C11	0.3726(2)	0.2541(2)	-0.0796(3)
C12	0.3912(2)	0.2105(2)	-0.1708(3)
C13	0.3649(2)	0.1450(2)	-0.1660(3)
C14	0.3173(2)	0.1227(1)	-0.0711(3)
C15	0.1375(2)	0.0811(1)	-0.0030(2)
C16	0.1280(2)	0.0140(1)	-0.0267(2)
C21	0.0871(2)	0.1959(1)	-0.0531(2)
C22	0.1203(2)	0.2455(1)	-0.1420(3)
C24	0.1271(2)	0.1640(2)	-0.2883(2)
C25	0.0951(2)	0.1093(2)	-0.2070(2)
H2	0.005(2)	0.103(1)	0.136(2)
H3	-0.074(2)	0.087(1)	0.307(2)
H4	-0.016(2)	0.065(1)	0.492(3)
H5	0.138(2)	0.054(1)	0.496(2)
H6	0.216(1)	0.071(1)	0.329(2)
H8	0.257(1)	0.161(1)	0.199(2)
H10	0.311(1)	0.262(1)	0.086(2)
H11	0.395(2)	0.304(1)	-0.085(2)
H12	0.425(2)	0.228(1)	-0.239(3)
H13	0.376(2)	0.114(1)	-0.222(2)
H14	0.304(1)	0.078(1)	-0.063(2)
H16	0.093(1)	-0.003(1)	-0.090(2)
H21A	0.106(2)	0.206(1)	0.033(2)
H21B	0.022(2)	0.196(1)	-0.055(2)
H22A	0.183(1)	0.248(1)	-0.142(2)
H22B	0.092(2)	0.289(1)	-0.124(2)
H24A	0.190(2)	0.166(1)	-0.282(2)
H24B	0.106(2)	0.155(1)	-0.367(2)
H25A	0.127(2)	0.067(1)	-0.225(2)
H25B	0.029(2)	0.104(1)	-0.207(2)

0.1389 nm and 0.1402 nm, whereas in **7b** the corresponding bond lengths are 0.1345 nm, 0.1365 nm and 0.1389 nm, respectively. The torsional angles between the nitrogen atom of the amino moiety and of the nitro group are -32.9° (N9-C2-C1-N5) and 171.4° (N20-C15-C16-N17) for **6a** and **7b**, respectively. The nitro group of **6a** is -11.4° (O11-N9-C2-C1) out of plane with the double bond whereas this angle for the dimethylamino group is found to be -17.3° (C7-N5-C1-C2). For compound **7b** these torsional angles are -16.8° (O18-N17-C16-C15) and 152.7° (C25-N20-C15-C16), respectively.

The second product of the thermal reaction of **3f** exhibits two doublets at δ 53.2 and δ 52.6 in the ^{13}C NMR spectrum, which revealed a cyclic structure (Scheme 3 and Table VI). Singlets present at δ 150.4 and δ 111.0, which correspond to the chemical shifts reported for nitroenamines[37,42,43], in combination with the observed J_{trans} 1.5 Hz, fit well to the four-membered cyclic nitroenamine structure **8b**. The cyclobutene **3e** behaved similarly upon heating, and the corresponding compounds **7a** and **8a** were obtained.

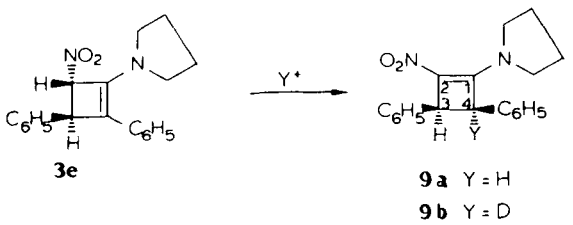
Surprisingly the 1,3-hydrogen shift (**3e,f** → **8a,b**) appears to be suprafacial. In terms of the *Woodward–Hoffmann* rules only an antarafacial 1,3-hydrogen shift is allowed but this is sterically impossible in a four-membered ring [44a]. In order to determine the possible role of the solvent we prepared the cyclobutene **3g**, in which a deuterium atom is present at C-4. However, in this case the reaction could not be followed by ^1H NMR spectroscopy, because the ring proton coincides with morpholine absorptions. TLC showed that in this case the formation of butadiene **7c** was the major reaction. This might be due to an isotope effect, making the rate of deuterium transfer in **3g** slower than that of the hydrogen atom in **3f**.

Upon heating (**8a**) or (**8b**) for 1 h at 80°C, only the corresponding butadienes **7a** and **7b**, respectively, were obtained. Butadiene derivatives arising from a scission of the C(3)-C(4) bond were not found, indicating the existence of an equilibrium between **3** and **8** (Scheme 3).

Although the cyclobutenes **3h-q** were fully characterized by MS spectrometry and IR, ^1H- and ^{13}C-NMR spectroscopy, the thermolysis of these compounds was not further studied because they all decompose and/or polymerize.

Reactivity of the cyclobutene **3e** *towards acid*

Upon treatment of the cyclobutene **3e** with acid in methanol, the orange colour of the crystals immediately changed to yellow. Mass spectrometry revealed that the obtained yellow compound was an isomer of the starting material. The ^{13}C NMR data of the compound were nearly identical with that found for the 2-nitrocyclobutenes **8** (Table VI). The ^1H NMR spectrum showed one major change. The protons of the reaction product of **3e** at δ 4.75 and δ 4.22 exhibit a much larger coupling constant, *viz.* 5.7 Hz than the starting material **3e**, and compounds **8a** and **8b** (1.5 Hz). Based upon the literature values for the coupling constants of *cis*-1,3-dinitro-2,4-diphenylcyclobutenes, reported by *Miller* and co-workers[25,34], we assigned the 2-nitrocyclobutene structure **9** to this compound, in which both ring protons are *cis*-oriented (Scheme 4). Consequently, the product **9** has also been formed by a 1,3-hydrogen shift. Treatment of **3e** with deuteriochloric acid in methanol-d_4 established that this 1,3-hydrogen shift was mediated by acid and/or the solvent, because the 2-nitrocyclobutene **9b**, in which one deuterium atom is incorporated at the C-4 position in the cyclobutene ring system, was obtained (Scheme 4).



3e

9a Y = H
9b Y = D

Scheme 4

When the nitrocyclobutenes **3e** or **8a** were dissolved in acetonitrile-d_3 and one drop of concentrated hydrochloric acid was added, the ^1H NMR spectra changed immediately. After 100 min at room temperature the ^1H NMR spectra of the compounds were identical and in both cases cyclobutene **9a** was formed.

A 1,3-hydrogen or a 1,3-halogen shift has also been observed in the (2 + 2) cycloadducts of ynamines with α,β-unsaturated esters[44b], α,β-unsaturated nitriles[44c], 2-cycloalkenones[44d,e] and α-halo-α,β-unsaturated nitriles[44f,g]. The driving force for this 1,3-hydrogen or 1,3-halogen migration is the increased conjugation of the enamine function and the electron-withdrawing moiety. It is obvious from our results that the nitroenamine system behaves similarly.

In the ^1H NMR spectrum of compounds **8** and **9** the CH_2 absorptions of the morpholine and pyrrolidine group appear as four separated multiplets, whereas in **3** these protons are present as two separated multiplets. Undoubtedly this is caused by restricted rotation around the carbon–nitrogen bond due to its partial double bond character. In the ^{13}C NMR spectra a very large difference between the chemical shifts of C-1 and C-2 indicates a considerable polarization of the double bond, consistent with an appreciable contribution of a strongly polarized resonance structure. On the basis of some literature data it is possible to compare four enamine systems: $R^4R^5N-C_\alpha=C_\beta-CN$[44g], $R^4R^5N-C_\alpha=C_\beta-COOMe$[22], $R^4R^5N-C_\alpha=C_\beta-NO_2$ and $R^4R^5N-C_\alpha=C_\beta-Ph$. The difference in chemical shifts of C_α and C_β is 86, 66, 40 and 29 ppm, respectively.

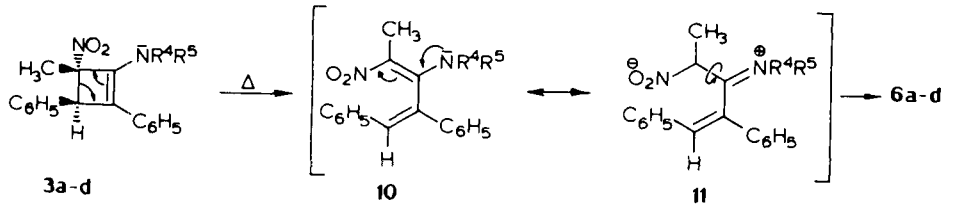
Discussion

In 1978 *Carpenter*[14] presented a model for predicting the effect of substituents on the rates of thermal pericyclic reactions. For cyclobutenes, depending on the substituents, *i.e.* polar groups or conjugative groups at C-1 and C-4, a disrotatory ring opening can be the low-energy pathway. Moreover, it has been accepted that due to steric factors bulky groups rotate outward if possible. However, *Dolbier* et al.[20] have shown that upon thermal ring opening of *trans*-perfluoro-3,4-dimethylcyclobutene the two bulky trifluoromethyl groups rotate inward. Therefore, it can be concluded that the electron-donating or electron-withdrawing properties of the substituents have a dominant influence on the ring opening. The occupied or empty orbitals, depending on the substituent, can mix with the LUMO or the HOMO of the cyclobutene[16]. The formation of the 1,3-dienes **6a-d**, *i.e.* the products obtained by a seemingly disrotatory cyclobutene-ring opening of **3a-d**, might be rationalized by this theory. In our case we have en electron-withdrawing nitro moiety at the sp^3-hybridized ring atom that seemed to have the properties discussed by *Carpenter*[14]. However, upon thermal ring opening of the cyclobutenes **3e,f** we obtained the products **7a,b**, which can have been formed by conrotatory ring opening of the cyclobutenes in such a way that both the bulky nitro and phenyl groups initially rotate inward. This leads subsequently to the thermodynamically favoured all-*trans*[45] configuration.

The only structural difference between the cyclobutenes **3a** and **3f** is the methyl substituent at C-4. The formation of different products upon thermal isomerization might be explained by the fact that the substituents of compound **7b** are in the all-*trans* configuration in which the conjugation between both the phenyl groups and between the nitro and the amine moiety is maximal.

However, it is possible to suggest an alternative explanation for the formation of the products **6** obtained by a seemingly disrotatory cyclobutene ring opening. Thermal treatment of **3a-d** can initially lead to a product in which the nitro moiety and the phenyl group have turned inward by a conrotatory process. The resonance structure (**11**) shows the partial single-bond character of the nitroenamine double bond. Rotation around this bond will yield the 1,3-dienes **6** (Scheme 5)[46].

From Table IV it can be concluded that the thermal stability of 4-nitro-1-cyclobuten-1-amines (**3a-d**) decreases in the order: $NEt_2 > N(CH_2)_4 > N(CH_2CH_2)_2O > NMe_2$. This means that not only the electron-donating properties of the amine function are important in the cyclobutene ring



3a-d **10** **11**

Scheme 5

opening, but probably also steric factors. This conclusion seems to be supported by the fact that in the case of ynamines the diethylamino group is a better electron-donor than the morpholinyl group[47].

The thermal ring opening of cyclobutenes annelated with a six- or an eight-membered ring normally proceeds at temperatures above 250°C[21]. In the bicycloalkenes **3i,j** the influence of the polar moiety at the ring system was apparent from the observation of reaction at only 80°C. However, in our case we were not able to isolate the reaction products. The bicyclo[3.2.0]hept-6-ene ring system (**3h**), *i.e.* a five-ring–four-ring annelation seems to be very stable (3 d at 80°C); in this case a conrotatory mode of ring opening is obviously not possible[21].

The 2-nitrocyclobutene, obtained from the thermal isomerization of the 4-nitro-1-cyclobuten-1-amines (**3**; R^1 = H), the *trans-N,N*-dialkyl-2-nitro-1-cyclobuten-1-amines **8**, results from a 1,3-hydrogen shift probably mediated by the solvent.

The formation of the *cis*-2-nitrocyclobutenes **9** is apparently sterically controlled by the phenyl moiety at C-3. The protons solvated by methanol can only approach from the sterically less hindered side. In the literature a 1,3-hydrogen migration has been reported for cyclobutenes bearing a strongly electron-withdrawing moiety at C-4[44]. The 1,3-hydrogen shift is not always stereoselective, because a mixture of *cis*- and *trans*-rearranged products was obtained from cyanosubstituted (2 + 2) cycloadducts in the presence of a catalytic amount of water[44d].

In conclusion, thermal treatment of the 4-nitro-1-cyclobuten-1-amines **3a-f** yields the 1,3-dienes **6a-f**, the formation of which follows the *Woodward–Hoffmann* rules. The formation of **6a-d** is attributed to *E/Z* isomerization of the enamine double bond of the product, initially formed by a conrotatory ring opening.

Experimental

Melting points were determined using a Reichert melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded using a Bruker WP-80 spectrometer and ^{13}C NMR spectra were recorded using a Nicolet NT 200-WB spectrometer, unless stated otherwise. The NMR spectra were recorded in $CDCl_3$, using tetramethylsilane (TMS) as an internal standard, unless stated otherwise. The thermal ring opening of **3** was monitored on the Bruker WP-80 spectrometer. Mass spectra (70 eV) were obtained using a Varian MAT 311A spectrometer and IR spectra using a Perkin-Elmer 257 spectrophotometer. X-Ray data of **3a**, **6a** and **7b** were obtained using an ENRAF-NONIUS CAD4 diffractometer. X-Ray data of **3f** were obtained using a Philips PW1100 diffractometer. Elemental analyses were carried out by *E. Hoogendam* and *A. Christenhusz* of the Laboratory of Chemical Analysis at the University of Twente.

Materials

The nitroalkenes **1a,b**[30], **1c,d**, **1i-k**[48,49], **1e,f**[50], **1g**[51] and **1h**[31], the ynamines **2a-f**[52,53], the cyclobutenes 1-(*trans*-4-methyl-4-nitro-2,3-diphenyl-1-cyclobuten-1-yl)pyrrolidine (**3b**) and 1-(*trans*-4-nitro-2,3-diphenyl-1-cyclobuten-1-yl)pyrrolidine (**3e**)[26] were prepared according to the literature. Chromatographic separations were performed on aluminum oxide (Al_2O_3) (E. Merck, neutral grade, particle size 0.063–0.300 mm, 70–230 mesh ASTM, activity IV). Petroleum ether refers to the fraction boiling at 60–80°C. All reactions were carried out in a nitrogen atmosphere. The mass spectra of **3k** and **3m** were calculated for ^{79}Br. Physical and spectral data of the nitrocyclobutenes **3** and **8–9**, and of the 1,3-dienes **6–7** are presented in Tables I, V and VI, respectively. The X-ray data of the nitrocyclobutenes **3a** and **3f**, and for the 1,3-dienes **6a** and **7b** are summarized in the Tables II-III and VII-VIII, respectively.

(E)-[2-($^2H_1$)-2-nitroethenyl]benzene (**1b**)

A solution of NaOD, prepared by dissolving sodium (0.69 g, 30.0 mmol) in deuterium oxide (9 ml), was added dropwise to a stirred solution of benzaldehyde (2.65 g, 25.0 mmol) and nitromethane-d_3 (1.60 g, 25.0 mmol) in methanol-d_4 (19 ml) at 0°C. The remaining white suspension was stirred for an additional $\frac{1}{2}$ h at 0°C. Subsequently the suspension was transferred into a dropping funnel and added dropwise to 2.5 M hydrochloric acid-*d* (20 ml). The yellow crystals formed were filtered and washed with water and subsequently recrystallized from methanol; yield 70%; m.p. 54–57°C (methanol). ^{1}H NMR: δ 7.98 (t, 1H, *J* 2.0 Hz). ^{13}C NMR: δ 136.8 (t, =CD). MS: accurate mass theor. for $C_8H_6DNO_2$ 150.054; exp. 150.055.

General procedure for the synthesis of the N,N-*dialkyl-4-nitro-1-cyclobuten-1-amines* **3**

A solution of the ynamine **2** (5.5 mmol) in dry acetonitrile (10 ml), dry tetrachloromethane (10 ml) or dry petroleum ether (10 ml) was added dropwise to a stirred suspension or solution of the nitroalkene **1** (5.0 mmol) in the same solvent (10 ml). When acetonitrile was used the addition of the ynamine was performed at 0°C. After the addition was complete the reaction mixture was stirred for an additional hour at 0°C, and subsequently allowed to reach room temperature. In most cases the reaction was complete after an additional 3–5 h stirring at room temperature. With petroleum ether or tetrachloromethane as a solvent the reaction mixture was usually stirred overnight at room temperature. If petroleum ether had been used a precipitate had formed which was collected by filtration. Trituration of the crude crystals with diisopropyl ether yielded the corresponding four-membered cyclic nitrones **4**. If acetonitrile or tetrachloromethane had been used as solvents, the reaction mixture was concentrated under reduced pressure at a temperature <25°C. Usually the four-membered cyclic nitrones **4** crystallized from the reaction mixture spontaneously. Otherwise the nitrones solidified upon addition of diisopropyl ether. The four-membered cyclic nitrones **4** were purified by trituration with diisopropyl ether[29]. Subsequently the filtrate was concentrated under reduced pressure. The viscous orange residue was purified by column chromatography (petroleum ether/diethyl ether, 1:1 v/v). The fractions with R_f 0.8–0.9 were collected, the solvent was allowed to evaporate at atmospheric pressure and room temperature and the *N,N*-dialkyl-4-nitro-1-cyclobuten-1-amines **3** were obtained as orange oils or solids.

(trans)-N,N,4-Trimethyl-4-nitro-2,3-diphenyl-1-cyclobuten-1-amine (**3a**). The reaction of nitroalkene **1c** and ynamine **2a** was performed in acetonitrile (it was found that in tetrachloromethane the reaction proceeded very slowly). The crude reaction mixture was concentrated under reduced pressure; upon addition of diisopropyl ether the oil solidified. Unfortunately the solid contained both nitrone and cyclobutene. Therefore, the solid was transferred into a small column-chromatography tube. Petroleum ether/diethyl ether (1:1 v/v) was dripped onto the solid. The solution that passed through the column was collected and after evaporation of the solvent under reduced pressure compound **3a** was obtained as an orange solid in a yield of 75%; m.p. 124–126° dec (chloroform/petroleum ether). Anal. calcd. for $C_{19}H_{20}N_2O_2$ (308.38): C 74.00, H 6.54, N 9.08; found: C 73.96, H 6.76, N 9.23%.

trans-N,N-Diethyl-4-methyl-4-nitro-2,3-diphenyl-1-cyclobuten-1-amine (**3c**). After reaction of nitroalkene **1c** and ynamine **2c** in acetonitrile as a solvent, column chromatography was applied to purify the cyclobutene. **3c** was obtained as an orange oil in a yield of 40%.

4-(trans-4-Methyl-4-nitro-2,3-diphenyl-1-cyclobuten-1-yl)morpholine (**3d**). After reaction of nitroalkene **1c** and ynamine **2d** in acetonitrile, the concentrated filtrate was submitted to column chromatography, to yield **3d** as an orange oil in a yield of 29%. Upon prolonged elution with diethyl ether a second product was isolated in addition to **3d**, *viz. (Z,Z)-4-[2-nitro-1-(1,2-diphenylethenyl)-1-propenyl]morpholine* (**6d**), which was obtained as a yellow solid in a yield of 22% *(vide infra)*.

4-(trans-4-Nitro-2,3-diphenyl-1-cyclobuten-1-yl)morpholine (**3f**). In this case the general procedure was slightly modified. A solution of nitroalkene **1a** in dry petroleum ether was added to a solution of ynamine **2d** in dry petroleum ether. When acetonitrile was used as a solvent no cyclobutene could be isolated from the reaction

mixture. Compound **3f** was obtained as an orange solid, in a yield of 12%; m.p. 124–130°C dec (diethyl ether/petroleum ether). Anal. calcd. for $C_{20}H_{20}N_2O_3$ (336.39): C 71.41, H 5.99, N 8.33; found: C 71.09, H 5.89, N 8.06%.

*4-[*trans*-4-($^2H_1$)-4-Nitro-2,3-diphenyl-1-cyclobuten-1-yl]morpholine* (**3g**). Ynamine **2d** was added in one portion to a suspension of nitroalkene **1b** in dry petroleum ether. The reaction mixture was stirred for 21 h at room temperature. Subsequently, filtration of the solid yielded a ± 1.3:1 mixture of the cyclobutene **3g** and the corresponding four-membered cyclic nitrone, according to ^{1}H NMR spectroscopy, respectively. The nitrone and the cyclobutene were separated by trituration of the solid with diethyl ether. Cyclobutene **3g** was obtained from the filtrate as an orange solid upon evaporation of the diethyl ether under vacuum, yield 37%; m.p. 125–128°C (methanol). Anal. calcd. for $C_{20}H_{19}DN_2O_3$ (337.40): C 71.20, H 5.68, D 0.60, N 8.30; found: C 71.49, (H + D) 6.01, N 8.09%.

trans-N,N-*Dimethyl-5-nitro-7-phenylbicylo[3.2.0]hept-6-en-6-amine* (**3h**). A mixture of **1e** and **2a** was stirred for 5 h in tetrachloromethane. The tan precipitate formed, *4a,5,6,7-tetrahydro*-N,N-*-dimethyl-4-phenylcyclopent[c][1,2]oxazin-3-amine 1-oxide*[54] was filtered off. Nitrocyclobutene **3h** was obtained as an orange oil from the concentrated reaction mixture, which solidified after a few days upon storage at −20°C; yield 55%; 66–92°C dec (methanol). Anal. calcd. for $C_{15}H_{18}N_2O_2$ (258.32): C 69.74, H 7.02, N 10.84; found: C 69.46, H 7.29, N 10.75%.

trans-N,N-*Dimethyl-6-nitro-8-phenylbicyclo[4.2.0]oct-7-en-7-amine* (**3i**). A mixture of **1f** and **2a** was stirred for 3 days in petroleum ether. The reaction mixture was concentrated under vacuum, and afforded after chromatographic purification **3i** as an orange oil; yield 37%.

trans-N,N-*Dimethyl-8-nitro-10-phenylbicyclo[6.2.0]dec-9-en-9-amine* (**3j**). A mixture of **1g** and **2a** in acetonitrile was stirred for 3 h, whereupon the reaction mixture was concentrated under reduced pressure. Subsequent chromatographic purification yielded **3j** as an orange oil; yield 37%.

cis-*4-Bromo*-N,N-*dimethyl-4-nitro-2,3-diphenyl-1-cyclobuten-1-amine* (**3k**). Cyclobutene **3k** was obtained as an orange solid upon reaction of **1h** and **2a** in tetrachloromethane in a yield of 50%; m.p. 90–92°C dec (diethyl ether/petroleum ether). Anal. calcd. for $C_{18}H_{17}BrN_2O_2$ (373.25): C 57.92, H 4.59, N 7.51; found: C 58.20, H 4.67, N 7.50%.

trans-*3-(3-Bromophenyl)*-N,N-*diethyl-2,4-dimethyl-4-nitro-1-cyclobuten-1-amine* (**3m**). Upon reaction of **1i** and **2e** in acetonitrile, **3m** was obtained as an orange oil; yield 40%.

trans-N,N-*Diethyl-3-(2-methoxyphenyl)-2,4-dimethyl-4-nitro-1-cyclobuten-1-amine* (**3n**). Upon reaction of **1j** and **2e** in acetonitrile, **3n** was obtained as an orange oil; yield 35%.

trans-*3-(1,3-Benzodioxol-5-yl)*-N,N-*diethyl-2,4-dimethyl-4-nitro-1-cyclobuten-1-amine* (**3p**). Upon reaction of **1k** and **2e** in acetonitrile, **3p** was obtained as an orange oil; yield 30%.

trans-N-*2,4-Trimethyl-4-nitro*-N,*3-diphenyl-1-cyclobuten-1-amine* (**3q**). A mixture of **1c** and **2f** in acetonitrile was stirred for 2 days, whereupon the concentrated filtrate was submitted to column chromatography (petroleum ether/diethyl ether, 1:2 v/v) to yield a 1:1 mixture of the unreacted ynamine **2f** and the nitrocylobutene **3q** as an orange oil, which was not further purified.

Compounds **6–9**

(Z,E)-N,N-*Dimethyl-4-nitro-1,2-diphenyl-1,3-pentadien-3-amine* (**6a**). The 1,3-diene **6a** was obtained from the contents of the NMR tubes which were used to study the ring opening of the cyclobutene **3a**. The concentrated contents of the NMR tubes were submitted to column chromatography (petroleum ether/diethyl ether, 1:1 v/v; the polarity of the eluent was slowly increased by the addition of diethyl ether), and yielded **6a** as a yellow solid after evaporation of the eluent at room temperature at atmospheric pressure. M.p. 148–153°C dec (methanol/petroleum ether). IR (KBr): 1655, 1240 (NO_2) cm^{-1}. Anal. calcd. for $C_{19}H_{20}N_2O_2$ (308.28): C 74.00, H 6.54, N 9.08; found: C 74.02, H 6.74, N 9.05%.

(Z,Z)-1-[2-nitro-1-(1,2-diphenylethenyl)-1-propenyl]pyrrolidine (**6b**). Cyclobutene **3b** (0.18 g, 0.5 mmol) was dissolved in dry benzene (5 ml) and heated at 80°C for a period of 2 h. The reaction mixture was concentrated under reduced pressure and submitted to column chromatography (petroleum ether/diethyl ether, 1:1 v/v; the polarity of the eluent was slowly increased by the addition of diethyl ether) to afford **6b** after evaporation of the eluent under reduced pressure, in 83% yield; m.p. 147–150°C (methanol/petroleum ether). IR (KBr): 1550, 1260 (NO_2) cm^{-1}. Anal. calcd. for $C_{21}H_{22}N_2O_2$ (320.39): C 75.42, H 6.63, N 8.38; found: C 75.46, H 6.68, N 8.34%.

(Z,E)-N,N-*Diethyl-4-nitro-1,2-diphenyl-1,3-pentadien-3-amine* (**6c**). Cyclobutene **3c** (1.0 g, 3.0 mmol) was dissolved in toluene (5 ml) and heated at 100°C for a period of 1½ h. The concentrated reaction mixture was submitted to column chromatography (petroleum ether/diethyl ether, 1:1 v/v; the polarity of the eluent was slowly increased by the addition of diethyl ether) and afforded after evaporation of the eluent at room temperature **6c** as a yellow solid; yield 33%; m.p. 130–132°C (toluene). IR (KBr): 1540, 1230 (NO_2) cm^{-1}. Anal. calcd. for $C_{21}H_{24}N_2O_2$ (336.44): C 74.97, H 7.19, N 8.33; found: C 74.61, H 7.36, N 8.13%.

(Z,Z)-4-[2-nitro-1-(1,2-diphenylethenyl)-1-propenyl]morpholine (**6d**). Compound **6d** was isolated similarly from the contents of the NMR tubes as described for **6a**. M.p. 163–173°C (ethyl acetate/methanol). IR (KBr): 1550, 1380 (NO_2) cm^{-1}. Anal. calcd. for $C_{21}H_{22}N_2O_3$ (350.42): C 71.98, H 6.33, N 7.99; found: C 72.18, H 6.16, N 7.79%.

*1-(*trans*-2-Nitro-3,4-diphenyl-1-cyclobuten-1-yl)pyrrolidine* (**8a**) and *(Z,E)-1-[2-nitro-1-(1,2-diphenylethenyl)ethenyl]pyrrolidine* (**7a**). Cyclobutene **3e** (0.32 g, 1.0 mmol) was heated at 60°C in dry benzene (5 ml) for 1 h. Subsequently the reaction mixture was concentrated under reduced pressure and separated into two fractions by repeated elution on Al_2O_3 preparative TLC plates. A mixture of petroleum ether/diethyl ether (1:2 v/v) was used as the eluent. Cyclobutene **8a** was isolated from the fraction with R_f 0.42; yield 58%. IR (KBr): 1640, 1400 (NO_2) cm^{-1}. MS: accurate mass theory 320.153 for $C_{20}H_{20}N_3O_2$; exp. 320.152.
From the fraction with R_f 0.25, the 1,3-diene (**7a**) was isolated as a yellow solid, yield 31%; m.p. 152–157°C (methanol/petroleum ether). IR (KBr): 1535 (NO_2) cm^{-1}. Anal. calcd. for $C_{20}H_{20}N_2O_2$ (320.39): C 74.98, H 6.29, N 8.74; found: C 75.08, H 6.42, N 8.56%.

*4-(*trans*-2-Nitro-3,4-diphenyl-1-cyclobuten-1-yl)morpholine* (**8b**) and *(Z,E)-4-[2-nitro-1-(1,2-diphenylethenyl)ethenyl]morpholine* (**7b**). Cyclobutene **3f** (0.34 g, 1.0 mmol) was heated at 60°C in dry benzene (5 ml) for 1 h. Then the reaction mixture was concentrated under reduced pressure and submitted to column chromatography (petroleum ether/diethyl ether, 1:1 v/v, the polarity of the eluent was slowly increased by the addition of diethyl ether); cyclobutene **8b** was isolated as the fastest eluted compound; yield 42%; m.p. 124–130°C (dec) (diethyl ether/petroleum ether). IR (KBr): 1625 (C=C and NO_2) 1400 (NO_2) cm^{-1}. Anal. calcd. for $C_{20}H_{20}N_2O_3$ (336.39): C 71.41, H 5.99, N 8.33; found: C 71.09, H 5.89, N 8.06%.
As the slowest eluted compound 1,3-diene **7b** was isolated as a yellow solid upon evaporation of the eluent at room temperature at atmospheric pressure; yield 40%; m.p. 149–154°C (diethyl ether). IR (KBr): 1540 (NO_2) cm^{-1}. Anal. calcd. for $C_{20}H_{20}N_2O_3$ (336.39): C 71.41, H 5.99, N 8.33; found: C 71.47, H 6.19, N 8.38%.

*1-(*cis*-2-Nitro-3,4-diphenyl-1-cyclobuten-1-yl)pyrrolidine* (**9a**) was obtained as yellow crystals in a yield of 68% upon trituration of the orange crystals of nitrocyclobutene **3e** (0.19 g, 0.59 mmol) in methanol (1 ml) acidified with one drop of concentrated hydrochloric acid. M.p. 166–176°C (dec) (methanol). IR (KBr): 1640 (C=C and NO_2), 1410 (NO_2) cm^{-1}. Anal. calcd. for $C_{20}H_{20}N_2O_2$ (320.39): C 74.97, H 6.29, N 8.74; found: C 74.72, H 6.19, N 8.56%.

*1-[*cis*-4-($^2H_1$)-2-Nitro-3,4-diphenyl-1-cyclobuten-1-yl]pyrrolidine* (**9b**) was obtained as yellow crystals in a yield of 68% upon trituration of the orange crystals of nitrocyclobutene **3e** (0.19 g, 0.59 mmol) in methanol-d_4 (1 ml) acidified with one drop of concentrated hydrochloric acid-*d*. M.p. 177–183°C (methanol). Anal. calcd. for $C_{20}H_{19}DN_2O_2$ (321.40): C 74.74, H 5.96, D 0.63, N 8.72; found: C 74.80, (H + D) 6.25, N 8.69%.

X-Ray crystal structure analyses of **3a,f**, **6a** *and* **7b**

Crystals of **3a** belong to the monoclinic space group $P2_1/c$, with cell constants: a = 14.367(7), b = 9.965(5), c = 12.372(5) Å, β = 109.03(5)°, Z = 4, d_c = 1.128 g·cm^{-3}. Data were collected at

293(2) K, MoKα radiation, graphite monochromator, ω–2θ scan, $3 < \theta < 25°$, scan width (ω) 1.0 + 0.4 tgθ. The refinement of the crystal structure is based upon 2040 reflections with $I > 3\sigma(I)$. The final weighted R factor is 4.5% for 289 variables.

Crystals of **3f** belong to the monoclinic space group Cc, with cell constants: $a = 18.618(4)$, $b = 8.893(2)$, $c = 10.768(3)$ Å, $\beta = 105.37(2)°$, $Z = 4$, $d_c = 1.300\ g \cdot cm^{-3}$. Data were collected at 173(2) K, MoKα radiation, graphite monochromator, ω–2θ scan, $3 < \theta < 25°$, scan width (ω) 1.8 + 0.3 tgθ. The refinement of the crystal structure is based upon 1358 reflections with $I > 3\sigma(I)$. The final weighted R factor is 2.7% for 307 variables.

Crystals of **6a** belong to the orthorhombic space group $P2_12_12_1$, with cell constants: $a = 7.322(4)$, $b = 13.114(5)$, $c = 17.364(5)$ Å, $Z = 4$, $d_c = 1.274\ g \cdot cm^{-3}$. Data were collected at 293(2) K, MoKα radiation, graphite monochromator, ω–2θ scan, $3 < \theta < 22.5°$, scan width (ω) 1.2 + 0.3 tgθ. The refinement of the crystal structure is based upon 1047 reflections with $I > 3\sigma(I)$. The final weighted R factor is 2.6% for 289 variables. The absolute configuration has not been determined.

Crystals of **7b** belong to the orthorhombic space group $Pbca$, with cell constants: $a = 15.703(4)$, $b = 19.839(6)$, $c = 11.324(2)$ Å, $Z = 8$, $d_c = 1.267\ g \cdot cm^{-3}$. Data were collected at 293(2) K, MoKα radiation, graphite monochromator, ω–2θ scan, $3 < \theta < 22.5°$, scan width (ω) 1.2 + 0.34 tgθ.

The refinement of the crystal structure is based upon 1387 reflections with $I > 3\sigma(I)$. The final weighted R factor is 3.5% for 307 variables. The X-ray structures were solved by direct methods[55]. Calculations were done using the SDP package[56]. Parameters refined were scale factor, extinction parameter, positional and anisotropic thermal parameters for the non hydrogen atoms; positional and isotropic thermal parameters for the hydrogen atoms. Hydrogen atom positions were found from difference Fourier synthesis.

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[32] In an apolar solvent, *i.e.* petroleum ether (b.p. 60–80°C) or tetrachloromethane, the *N,N*-dialkyl-4-nitro-1-cyclobuten-1-amines **3** are the major products, whereas in a polar solvent, *i.e.* acetonitrile generally the four-membered cyclic nitrones **4** are the major products[26,29].
[33] The *N,N*-dialkyl-4-nitro-1-cyclobuten-1-amines (**3**; R^1 = Ph) could not be isolated. Although ^{1}H NMR spectroscopy of the crude reaction mixture indicated the possible presence of these cyclobutenes, neither cyclobutenes nor other analytically pure products were obtained by the normal work-up method.
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[38] The approximate half-life time of **3a-d** could be measured from the ^{1}H NMR spectra. The decrease of the H-3 and the CH_3C-4 signal of the compounds **3a-d** and the increase of the CH_3 signal of the compounds **6** were used as a probe. The ratio of the lengths of these peaks, *i.e.* length H-3 peak *versus* length CH_3 peak, and length CH_3C-4 peak *versus* length CH_3 peak, were used for the estimation of $t_{1/2}$.
[39] ^{1}H and ^{13}C NMR data of (*E*)-1-(2-nitroethenyl)morpholine of H-1, H-2, C-1 and C-2 are δ 8.17, 6.85, 149.4 and 112.8, respectively[43].
[40] H-1 of (*E*)-1,2-diphenylethene is found at δ 7.08 in the ^{1}H NMR spectrum. From "the Sadtler standard spectra", number 14717.
[41a] To explain the differences in stereochemistry of the nitroenamine system in the 1,3-dienes **6a** and **7b** we have performed

some MINDO calculations[41b] on three simple nitroenamine systems, *i.e.* (*E*)-*N,N*-dimethyl-2-nitroethenamine, (*E*)-*N,N*--dimethyl-2-nitropropen-1-amine, and (*Z*)-*N,N*-dimethyl-2-nitropropen-1-amine. The calculations showed that the introduction of a methyl group at C-2 has a large effect on the stereochemistry of the nitroenamine system. In the absence of the methyl group both polar substituents are parallel with the double bond, *i.e.* the molecule is flat, whereas in the presence of the methyl group both dimethylamino and nitro moiety are perpendicular to the double bond, and thus probably a diminished conjugation is found between both groups. A small effect on the bond order was also found, *i.e.* in the absence of the methyl group the conjugation between the dimethylamino and the nitro moiety is relatively larger;

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