Cycloadditions of Nitrile Oxides to the Highly Reactive *N*-Acyl-2-oxa-3-azanorborn-5-enes Afford Versatile Cycloadducts and a Convenient Entry to Highly Functionalized Derivatives

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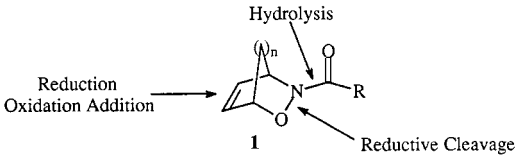
N-Acyl-2-oxa-3-azanorborn-5-enes are highly reactive dipolarophiles in cycloadditions with nitrile oxides. The cycloadducts can be easily elaborated to various functionalized structures that are not directly accessible by 1,3-dipolar cycloadditions.

Introduction

Nitrosocarbonyl intermediates are versatile synthetic tools because of their high reactivity in hetero Diels−Alder (HDA) cycloadditions and the synthetic potential of their HDA adducts.[1−3] The highly stereo- and regioselective outcomes of their HDA cycloadditions have been extensively investigated and the HDA adducts **1** have been widely used in different synthetic operations, allowing for the flexible introduction of multifunctionality. The *N*-acyl substituent can be detached under mild conditions[4] while several methods are available to cleave reductively the N−O bond of the adducts, including the use of amalgams [Na(Hg), Al(Hg)],[5] metals in acids (Zn/AcOH, Zn/HCl) or catalytic hydrogenation.[6]



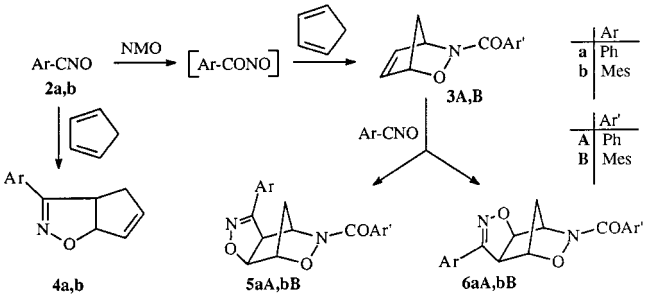
Many examples are known of elaborations of the unsaturated moiety of **1**. Oxidations with OsO_4/*N*-methylmorpholine *N*-oxide (NMO)[4,5] and *m*-chloroperbenzoic acid (*m*CPBA)[7] have been reported, as have reductions with diimide.[8] A single example of a [4+2] cycloaddition of 1,3-butadiene to the 1,3-cyclohexadiene adducts of nitrosocarbonyl intermediates was described by Boger.[9]

Nitrosocarbonyl intermediates are commonly generated by oxidation of hydroxamic acids with periodate salts, and the search for more selective oxidants is being actively pursued.[10] We have recently developed a convenient alternative procedure for the generation of nitrosocarbonyl intermediatess by the mild oxidation of nitrile oxides with tertiary amine *N*-oxides.[11] We report a study of the cycloadditions of nitrile oxides to the unsaturated moiety of the HDA adducts **1** derived from the cycloaddition of nitrosocarbonyl intermediates to cyclopentadiene. These derivatives proved to be highly reactive dipolarophiles in the 1,3-dipolar cycloadditions of nitrile oxides, and the cycloadducts were elaborated into highly functionalized structures which are not directly accessible by 1,3-dipolar cycloadditions.

Results

The High Dipolarophilic Activity of Oxazanorbornenes 3

We obtained the *N*-acyl-oxazanorbornenes **3A**,**B** by the mild oxidation of benzonitrile oxide (BNO) (**2a**) and mesitonitrile oxide (MNO) (**2b**) in CH_2Cl_2 with NMO in the presence of a slight excess of cyclopentadiene (1.5 equivalents) according to a published procedure (Scheme 1).[11] In the case of cyclohexadiene, the yields of the nitrosocarbonyl adducts analogous to **3A**,**B** were excellent and the only detectable by-products were the 1,3-dipolar cycloadducts of the nitrile oxides to cyclohexadiene.[11b] In the experiments performed with cyclopentadiene, the yields of the nitrosocarbonyl adducts **3A**,**B** were somewhat lower and we could now identify as by-products the 1,3-dipolar cycloadducts **5aA**,**bB** and **6aA**,**bB** along with the 1,3-dipolar cycloadducts to cyclopentadiene **4a**,**b**.



Scheme 1

Table 1 gives the product distributions for the trapping of nitrosocarbonyl intermediates with cyclopentadiene with different reactant ratios. With NMO (1.5 equivalents) and a slight excess of cyclopentadiene (1.5 equivalents), fair yields of the nitrosocarbonyl adducts **3** were observed,

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along with observable amounts of the products **5** and **6** of their further reaction. Upon increasing the excess of the diene, the amounts of the 1,3-dipolar cycloadducts to the diene **4a**,**b** increase progressively because of the increased competition to the oxidation step of the nitrile oxide presented by the 1,3-dipolar cycloaddition of the nitrile oxide to cyclopentadiene. Correspondingly, the yields of the nitrosocarbonyl adducts **3** and the products of their further reaction **5** and **6** drop appreciably. On the other hand, the increase in NMO equivalents (Entries 4, 8) can remedy this drop by increasing the oxidation rate. A similar trend was reported[11b] for the trapping of nitrosocarbonyl intermediates with cyclohexadiene. In the cyclohexadiene case, however, the nitrosocarbonyl adducts analogous to **3** display only a low dipolarophilic activity, typical[12] for the bicyclo[2.2.2]oct-2-ene derivatives, and the products of their further reaction with nitrile oxides were not formed in appreciable amounts under these conditions.

Table 1. Dependence of product distribution upon reactant ratio in the trapping of nitrosocarbonyl intermediates with cyclopentadiene

Entry	NMO equiv.	Cyclopentadiene equiv.	**3**	**4**	**5** + **6**
Ar = Ph					
1	1.5	1.5	89	1	10
2	1.5	6	88	4	8
3	1.5	30	64	29	7
4	6	30	87	4	9
Ar = Mes					
5	1.5	1.5	87	1	12
6	1.5	6	82	9	9
7	1.5	30	54	39	7
8	6	30	81	7	12

As a whole, the results show that the *N*-acyl-oxazanorbornene derivatives **3** are highly reactive dipolarophiles toward nitrile oxides and are by far more reactive than cyclopentadiene.

We have performed a few competition experiments with the *N*-benzoyl derivative **3A** and norbornene, a well-known highly reactive dipolarophile.[12,13] Somewhat unexpectedly, **3A** is 1.7 times more reactive than norbornene itself towards BNO and 1.5 times more reactive towards MNO, in spite of the presence of the two electronegative allylic substituents, which should lower the energies of the frontier orbitals (FO) and thus reduce the reactivity in cycloadditions with the moderately electrophilic nitrile oxides.

Structures of the Adducts 5 and 6

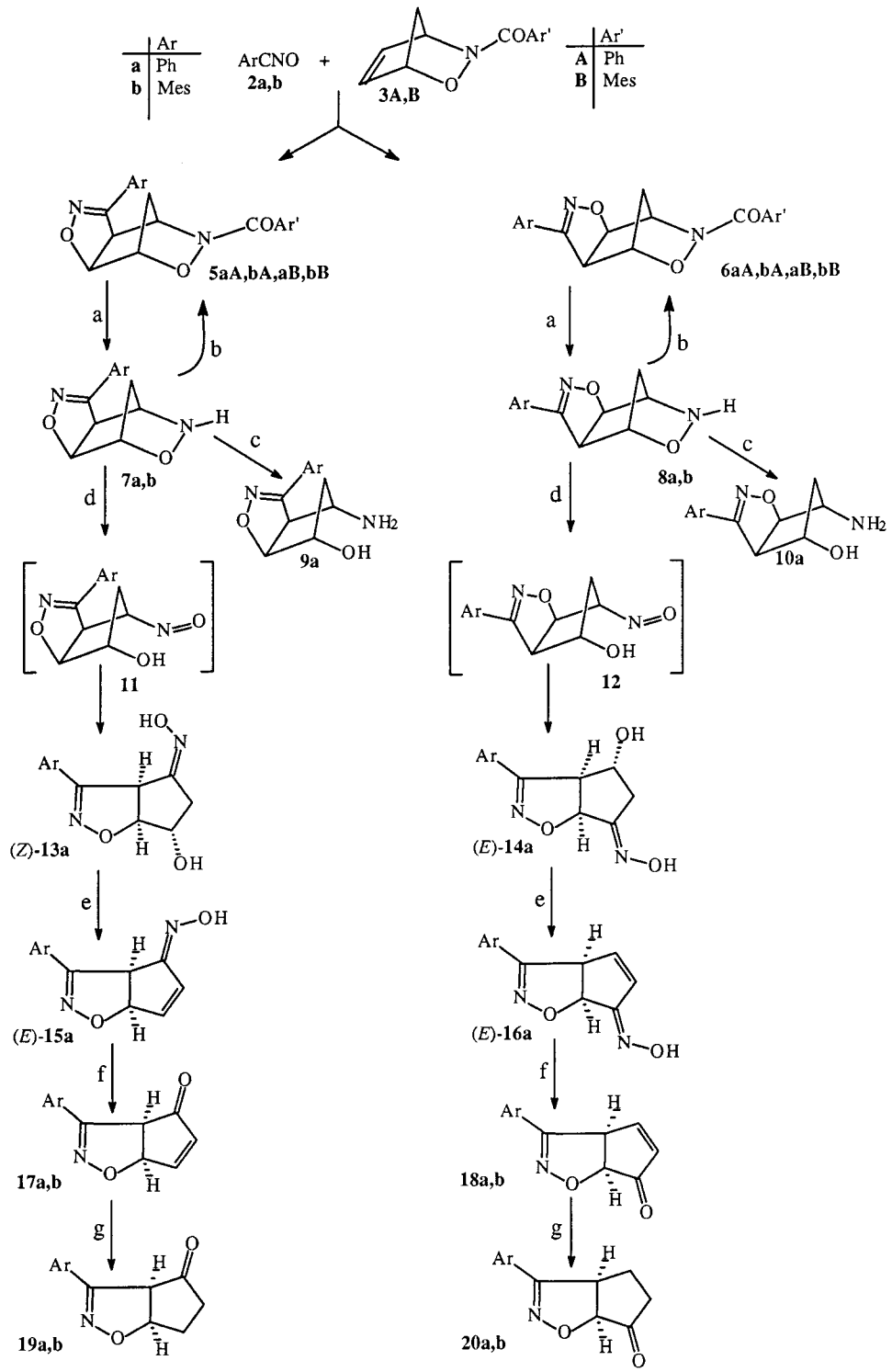
The adducts **5** and **6** were obtained by cycloaddition of nitrile oxides **2a**,**b** with a slight excess of the *N*-acyl-2-oxa-3-azabicyclo[2.2.1]hept-5-enes **3** (1.1 equiv.) in almost quantitative yields. Generation of BNO (**2a**) in benzene in the presence of the *N*-benzoyloxazanorbornene **3A** afforded a 3:2 mixture of the two adducts **5aA** and **6aA**, which were easily separated from each other by column chromatography. The NMR spectra are fully consistent with the *exo* structure of the adducts; the lack of appreciable coupling between the isoxazoline and the bridgehead protons is typical of norbornene *exo* adducts.[14] Nevertheless, the spectra do not permit any regiochemical assignment, that was firmly established with the aid of the transformations reported in Scheme 2.

Alkaline hydrolysis of the adducts takes place easily (NaOH/MeOH, room temp., 12 h) and affords the cyclic hydroxylamines **7a** and **8a**, which were converted by catalytic hydrogenation (Pd/C, AcOEt) to the aminols **9a** and **10a**. Again, the NMR spectra do not allow any sharp distinction between the isomeric aminols, because of the lack of appreciable coupling between the isoxazoline and the vicinal methine protons. This is presumably due to the adoption of the envelope conformation, sketched in the formulas of Scheme 2, aided by the intramolecular hydrogen bond between the alcoholic and amino moieties. On the other hand, oxidative cleavage of the hydroxylamine bond of **7a** and **8a** with *m*CPBA in methanol in the presence of a suitable isomerization catalyst (NaOAc)[15] also takes place easily, affording in excellent yields mixtures of the (*E*)- and (*Z*)-oximes **13a** and **14a**, deriving from the isomerization of the intermediate nitroso alcohols **11** and **12**. The stereochemical assignments for the (*E*/*Z*) oxime pairs rely upon the characteristic deshielding of the protons proximal to the oxime hydroxy group[16] and the major stereoisomers are shown in Scheme 1. Acidic hydrolysis of the oximes **13a** and **14a** affords at first mixtures of the unsaturated (*E*)- and (*Z*)-oximes **15a** and **16a** and then the unsaturated ketones **17a** and **18a**. Catalytic hydrogenation of the latter compounds afforded the saturated ketones **19a** and **20a**, identical to authentic specimens whose regiochemical assignment is firmly based on the multiplicity of the isoxazoline protons.[17]

The stable MNO (**2b**) similarly adds easily to **3A**. The reaction is over in a few hours at room temp. and affords a mixture of the cycloadducts **4bA** and **5bA** in a 52:48 ratio. The adducts were hydrolyzed to the cyclic hydroxylamines **7b** and **8b** and converted into the saturated ketones **19b**[17] and **20b**. The latter ketone **20b** could be identified in the cycloaddition mixture of MNO and 2-cyclopenten-1-one, where the ketones **19b** and **20b** are formed in a 96:4 ratio.

Cycloadditions of BNO and MNO to the *N*-mesitoyl derivative **3B** were also performed, yielding mixtures of the BNO adducts **5aB** and **6aB** and MNO adducts **5bB** and **6bB** in an approximately 1:1 ratio. Alkaline detachment of the *N*-mesitoyl substituent does not take place easily in these cases and the regiochemistry was established with an independent synthesis of the adducts by acylation of the cyclic hydroxylamines **7a**,**b** and **8a**,**b** with mesitoyl chloride.

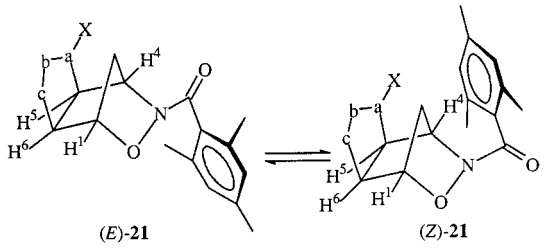
While the NMR spectra of the *N*-benzoyloxazanorbornene **3A** and its adducts **5Aa**,**b** and **6Aa**,**b** exhibit only line broadenings due to the restricted rotation of the benzoyl substituent about the C−N bond, usual for *O*,*N*-dialkylhydroxamic acids,[18] the *N*-mesitoyl-oxazanorbornene **3B** and its adducts **6Ba**,**b** show two sets of signals, which can be ascribed to the presence of the two rotamers (*E*)-**21** and (*Z*)-**21** in slow equilibrium and in approximately equal amounts. In the regioisomeric adduct **5aB**, on the other hand, the (*E*) and (*Z*) rotamers are present in a 2:1 ratio



Scheme 2. Conditions for **5A** and **6A**: a) NaOH/MeOH, room temp. 12 h, 72−80%; b) Ar′COCl, Et_3N, CH_2Cl_2, room temp. 12 h, 70−80%; c) H_2, Pd/C, AcOEt, room temp. 10 min, 60−73%; d) *m*CPBA, NaOAc, MeOH, room temp. 12 h, 76−90%;− e) C_6H_6, TsOH, ΔT, 1 h, 70%; f) 5% HCl, ΔT, 2 h, 63−75%; g) H_2, Pd/C, AcOEt, room temp. 1 h, quant.

while the dimesityl adduct **5bB** shows a single set of signals attributable to the (*E*) rotamer.

The increase in the barrier to rotation for the 2,4,6-trimethylphenyl substituent is well precedented in the case of amides[19] and the assignment of signals to the (*E*) and (*Z*) rotamers could be based on the sizeable anisotropic effects of the amide group,[19] which cause deshielding of the hydrogen atoms proximal to the carbonyl oxygen atom and shielding of the hydrogen atoms proximal to the orthogonal 2,4,6-trimethylphenyl ring. Thus, the two rotamers exhibit similar energies in general, but the presence of a phenyl or the bulkier 2,4,6-trimethylphenyl group in the position



marked with an X in **21** causes steric hindrance in (*Z*)-**21** and shifts the equilibrium towards the (*E*) rotamer in **5aB** [(*E*)/(*Z*) = 2:1] and, even more so, in **5bB**, where only the signals of the (*E*) rotamer appear. The assignments were established with the aid of the ^{13}C-NMR spectra, which show the C1−O signals in the expected range (δ = 79−82), while the C4−N signals are well separated and appear at δ = 55−63. They were corroborated by the appropriated ^{13}C-^{1}H COSY (HSQC) experiments.[20]

Discussion

The *N*-acyl-2-oxa-3-azanorbornenes **3** are quite reactive dipolarophiles in 1,3-dipolar cycloadditions with nitrile oxides. The cycloadditions take place stereospecifically on the *exo* face and rather unselectively afford mixtures of the two regioisomeric cycloadducts **5** and **6**. This lack of selectivity is due to the comparable electron-withdrawing abilities of the alkoxy and acylamino allylic substituents, which have similar σ_I substituent constants.[21] The adducts can be easily manipulated and the reductive or oxidative cleavage of the hydroxylamine bond of the deacylated cyclic hydroxylamines **7** and **8** provide convenient routes to stereodefined and highly functionalized structures which are not accessible by direct cycloaddition. The α,β-unsaturated ketones **17** and **18** are formal adducts of nitrile oxides to the elusive cyclopentadienone and are valuable intermediates for further elaboration. The chemistry of the related formal diene adducts to cyclopentadienones has been extensively investigated and used in many synthetic applications.[22]

The *N*-acyl-2-oxa-3-azanorbornenes **3** closely resemble the parent norbornene in reactivity. The origin of the high reactivity of norbornene and the exclusive *exo* selectivity of its reactions has attracted a great deal of attention[12,23] and is usually attributed to relief of strain,[24] geometric deformation of the double bond (pyramidalization due to π/σ repulsions)[25] and also favourable staggering effects for the *exo* attacks.[26]

Contrary to expectations based on FO interactions, the *N*-acyl-2-oxa-3-azanorbornenes are even better dipolarophiles than norbornene itself. We believe that the higher reactivity of the *N*-acyl-2-oxa-3-azanorbornenes has to be related to an enhancement of the intrinsic factors which determine the reactivity of norbornene; in the case at hand relief of strain[24] and geometric deformation of the double bond.[25] In Figure 1 we have sketched the shapes of norbornene (**22**)[27] and the more stable conformer[28] of *N*-formyl-2-oxa-3-azanorbornene (**23**) as obtained with a STO-3G geometry optimization.

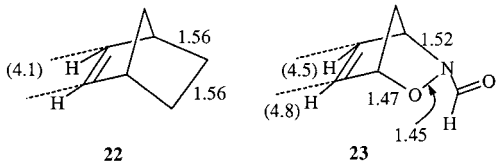


Figure 1. Geometric features of the STO-3G-optimized structures of norbornene and *N*-formyl-2-oxa-3-azanorbornene; numbers near the bonds are bond lengths in Å and numbers in parentheses near the hydrogen atoms specify the out-of-plane angles of the corresponding hydrogen atoms in degrees

As shown in Figure 1, the replacement of the CH_2CH_2 bridge in **22** with O−N(CHO) in **23** causes a shortening of the two-membered saturated bridge because of the shorter C−O, N−O and N−C bonds and this should induce additional strain in the hetero-substituted structure **23**. Moreover, the deformation of the double bond, with tilting of the vinyl hydrogen atoms away from the *exo* region, increases on going from norbornene (**22**) to the hetero-substituted derivative **23** since this tilting maximizes the more efficient stabilizing π-σ*$_{CO}$ and π-σ*$_{CN}$ interactions.[29]

Conclusion

We have reported here an example of a 1,3-dipolar cycloaddition of nitrosocarbonyl adducts to cyclopentadiene. The *N*-acyl-2-oxa-3-azanorbornenes are indeed quite interesting dipolarophiles. They can be prepared in simple ways and are highly reactive dipolarophiles. More interestingly, their adducts can be transformed in a variety of ways, affording otherwise inaccessible structures in a stereocontrolled manner. From a mechanistic point of view, the results fully clarify the complex course of the reaction of cyclopentadiene with nitrosocarbonyl intermediates generated according to the nitrile oxide route. Because of their high dipolarophilic activities, the nitrosocarbonyl adducts to cyclopentadiene easily enter into subsequent reactions with the reactants.

Experimental Section

General: All melting points are uncorrected. Elemental analyses were performed with a C. Erba 1106 elemental analyzer. − ^{1}H- and ^{13}C-NMR spectra were recorded with a Bruker AVANCE 300 spectrometer in $CDCl_3$ solutions unless otherwise stated. Chemical shifts are expressed in ppm from internal tetramethylsilane (δ). − IR spectra (nujol mulls) were recorded with an FT-IR Perkin−Elmer Paragon 1000. − Column chromatography and TLC: silica gel H60 and GF_{254} (Merck), respectively, eluent cyclohexane/ethyl acetate (9:1 to 5:5). The identification of samples from different experiments was accomplished by mixed mps and superimposable IR spectra.

Materials: Benzhydroximoyl chloride, the precursor of BNO (**2a**),[30] was obtained by treatment of benzaldoxime with sodium hypochlorite[31] and mesitonitrile oxide (**2b**) by oxidation of 2,4,6-trimethylbenzaldoxime with bromine.[32] The *N*-acyl-2-oxa-3-azab-

icyclo[2.2.1]hept-5-enes **3A** and **3B** were obtained by the mild oxidation of nitrile oxides **2a** and **2b** with NMO in the presence of cyclopentadiene.[11] The BNO and MNO adducts with norbornene and the BNO adduct **4a** with cyclopentadiene were available from previous work.[11b] The MNO adduct **4b** with cyclopentadiene was obtained by adding MNO (0.3 g) to excess cyclopentadiene (5 equiv.) in benzene (20 mL). After keeping for 1 d at room temp., the solvent was removed. Column chromatography afforded **4b** (86%), m.p. 45−46 °C from petroleum ether. − ^{1}H NMR: δ = 2.19 (s, 6 H, *o*,*o*′-CH_3), 2.31 (s, 3 H, *p*-CH_3), 2.27−2.61 (m, 2 H, CH_2), 4.15 (m, 1 H, 4-isoxazoline H), 5.80 (m, 1 H, 5-isoxazoline H), 5.90 and 6.04 (m, 2 H, C*H*=C*H*), 6.91 (s, 2 H, arom.). − ^{13}C NMR: δ = 19.8 (*o*,*o*′-CH_3), 20.9 (*p*-CH_3), 34.8 (CH_2), 52.2 (C-4), 89.2 (C-5), 125.9, 128.5, 136.9, 138.4 (C-arom.), 130.1, 133.2 (CH=CH), 158.8 (C=N). − $C_{15}H_{17}NO$ (227.3): calcd. C 79.26, H 7.54, N 6.16; found C 79.2, H 7.6, N 6.3.

Cycloadditions of Nitrile Oxides 2a,b to the *N*-acyl-2-oxa-3-azabicyclo[2.2.1]hept-5-enes 3A,B: BNO (**2a**) was generated in situ by dehydrohalogenation of benzhydroximoyl chloride with triethylamine.[30] To a stirred solution of benzhydroximoyl chloride (5 g, 32 mmol) and the dipolarophiles **3A,B** (35 mmol) in anhydrous benzene (100 mL), a solution of triethylamine (5 mL, 1.1 equiv.) in the same solvent (20 mL) was added over a period of 0.5 h. After keeping the reaction mixture for 2 d at room temp., triethylamine hydrochloride was filtered off and the filtrate was concentrated under reduced pressure, leaving a residue which was separated by column chromatography. Cycloadditions of MNO (**2b**) were performed by adding the dipolarophiles **3A**,**B** (11 mmol) to a stirred solution of mesitonitrile oxide (1.6 g, 10 mmol) in anhydrous benzene (100 mL). After keeping for 1d at room temp., the solvent was removed and the mixtures were separated by column chromatography. Elution afforded first the less polar cycloadducts **5** and then the regioisomeric ones **6**.

The physical and analytical data and the yields of the cycloadducts **5** and **6** are reported in Table 2 and the relevant NMR data are collected in Table 3.

Table 2. Physical and analytical data for adducts **5** and **6** of *N*-acyl-2-oxa-3-azanorbornenes **3**

	m.p. [°C] Solvent[a]	Yield [%] (ratio **5**/**6**)	Formula	C, H, N found (C, H, N calcd.)	$\tilde{\nu}_{C=O}$
5aA	181−182	56	$C_{19}H_{16}N_2O_3$	71.4, 5.0, 8.5	1643
6aA	160−161	37		71.3, 5.1, 8.6	1659
	B	(60:40)		(71.24, 5.03, 8.75)	
5bA	183−184	45	$C_{22}H_{22}N_2O_3$	72.8, 6.1, 7.6	1650
6bA	166−167	42		72.7, 6.0, 7.8	1673
	B/L	(52:48)		(72.91, 6.12, 7.73)	
5aB	84−85	48	$C_{22}H_{22}N_2O_3$	72.8, 6.2, 7.7	1667
6aB	142−143	39		72.7, 6.1, 7.9	1651
	B/L	(55:45)		(72.91, 6.12, 7.73)	
5bB	162−163	44	$C_{25}H_{28}N_2O_3$	74.1, 6.8, 6.8	1660
6bB	257−258	44		74.2, 7.1, 6.7	1667
	B/L	(50:50)		(74.23, 6.98, 6.93)	

[a] B: benzene, L: ligroin.

Alkaline Hydrolysis of the *N*-Benzoyl Adducts 5 and 6: The *N*-benzoyl adducts **5aA**,**B** and **6aA**,**B** were deacylated by adding the adducts (3 mmol) to a stirred solution of NaOH (5 mmol) in methanol (30 mL). After keeping overnight at room temp., the solutions were concentrated under reduced pressure. Dilution with water precipitated the insoluble cyclic hydroxylamines **7** and **8**, which were filtered or extracted with ethyl acetate:

Compound 7a: 80%, m.p. 94−95 °C from ethanol. − IR: $\tilde{\nu}$ = 3210 cm^{-1} (NH). − ^{1}H NMR: δ = 1.79 and 2.15 (d, *J* = 11.5 Hz, 2 H, CH_2), 4.06 (d, *J* = 8.3 Hz, 1 H, 5-H), 4.08 (s, 1 H, 4-H), 4.72 (s, 1 H, 1-H), 4.90 (d, *J* = 8.3 Hz, 1 H, 6-H), 5.65 (br. s, 1 H, NH), 7.45 (m, 3 H, arom.) and 7.76 (m, 2 H, arom.). − ^{13}C NMR: δ = 34.8 (CH_2), 56.0 (CH−N), 59.2 (C-4), 77.4 (CH−O), 83.6 (C-5), 126.7, 128.1, 128.9, 130.3 (C-arom.), 155.8 (C=N). − $C_{12}H_{12}N_2O_2$ (216.2): calcd. C 66.65, H 5.59, N 12.96; found C 66.5, H 5.5, N 12.8.

Compound 8a: 77%, m.p. 126−127 °C from benzene/ligroin. − IR: $\tilde{\nu}$ = 3240 cm^{-1} (NH). − ^{1}H NMR: δ = 1.83 and 2.15 (d, *J* = 12.0 Hz, 2 H, *CH*$_2$), 4.03 (d, *J* = 8.5 Hz, 1 H, 6-H), 4.1 (s, 1 H, 4-H), 4.78 (s, 1 H, 1-H), 5.0 (d, *J* = 8.5 Hz, 1 H, 5-H), 5.7 (br. s, 1 H, NH), 7.4 (m, 3 H, arom.) and 7.75 (m, 2 H, arom.). − ^{13}C NMR: δ = 34.5 (CH_2), 57.9 (CH−N), 61.5 (C-4), 76.4 (CH−O), 84.0 (C-5), 126.7, 128.1, 128.9, 130.3 (C-arom.), 155.3 (C=N). − $C_{12}H_{12}N_2O_2$ (216.2): calcd. C 66.65, H 5.59, N 12.96; found C 66.6, H 5.7, N 12.9.

Compound 7b: 72%, m.p. 169−170 °C from ethanol. − IR: $\tilde{\nu}$ = 3144 cm^{-1} (NH). − ^{1}H NMR: δ = 1.92 and 2.39 (d, *J* = 11.5 Hz, 2 H, CH_2), 2.29 (s, 6 H, *o*,*o*′-CH_3), 2.31 (s, 3 H, *p*-CH_3), 3.78 (s, 1 H, 4-H), 3.84 (d, *J* = 8.6 Hz, 1 H, 5-H), 4.76 (s, 1 H, 1-H), 4.89 (d, *J* = 8.6 Hz, 1 H, 6-H), 4.60 (br. s, 1 H, NH), 6.93 (s, 2 H, arom.). − ^{13}C NMR: δ = 20.2 (*o*,*o*′-CH_3), 20.9 (*p*-CH_3), 35.3 (CH_2), 58.8 (C-4), 60.1 (CH−N), 77.4 (CH−O), 82.8 (C-5), 124.9, 128.9, 136.4, 138.9 (C-arom.), 156.4 (C=N). − $C_{15}H_{18}N_2O_2$ (258.3): calcd. C 69.74, H 7.02, N 10.85; found C 69.9, H 6.9, N 10.9.

Compound 8b: 77%, m.p. 125−126 °C from benzene/ligroin. − IR: $\tilde{\nu}$ = 3218 cm^{-1} (NH) − ^{1}H NMR: δ = 1.92 and 2.38 (d, *J* = 11.2 Hz, 2 H, CH_2), 2.24 (s, 6 H, *o*,*o*′-CH_3), 2.29 (s, 3 H, *p*-CH_3), 3.78 (d, *J* = 8.2 Hz, 1 H, 6-H), 4.12 (s, 1 H, 4-H), 4.46 (s, 1 H, 1-H), 4.96 (d, *J* = 8.2 Hz, 1 H, 5-H), 5.7 (br. s, 1 H, NH), 6.90 (s, 2 H, arom.). − ^{13}C NMR: δ = 20.2 (*o*,*o*′-CH_3), 20.9 (*p*-CH_3), 34.9 (CH_2), 61.4 (CH−N), 61.9 (C-4), 76.1 (CH−O), 83.1 (C-5), 124.9, 128.8, 136.3, 138.9 (C-arom.), 155.9 (C=N). − $C_{15}H_{18}N_2O_2$ (258.3): calcd. C 69.74, H 7.02, N 10.85; found C 69.8, H 6.9, N 10.7.

Acylation of the hydroxylamines **7a**,**b** and **8a**,**b** with benzoyl chloride and 2,4,6-trimethylbenzoyl chloride afforded in fair yields the corresponding *N*-acyl derivatives, identical with the cycloadducts **5** and **6**. In a typical experiment, a slight excess of 2,4,6-trimethylbenzoyl chloride (0.11 g, 0.6 mmol) and triethylamine (0.14 mL, 1 mmol) were added to a solution of **7a** (0.1 g, 0.5 mmol) in CH_2Cl_2 (20 mL). After keeping overnight at room temp., the solution was diluted with CH_2Cl_2, washed with water, 5% $NaHCO_3$ and more water, dried with Na_2SO_4 and concentrated, leaving a residue which crystallized from ethanol to give adduct **5aB** in a 73% yield.

Hydrogenolysis of the Cyclic Hydroxylamine 7a,b and 8a,b: A solution of **7a** (1 mmol) and 10% Pd/C (0.03 g) in ethyl acetate (50 mL) absorbed 1 equiv. of hydrogen within 10 min. The catalyst was filtered off and the filtrate was concentrated under reduced pressure. Crystallization from benzene afforded the aminol **9a** (60%), m.p. 155−156 °C. − IR: $\tilde{\nu}$ = 3340, 3280 cm^{-1} (NH_2). − ^{1}H NMR: δ = 1.6 (br. s, 3 H, NH_2 and OH), 1.83 (m, 2 H, CH_2), 3.83 (br. s, 1 H, CH−N), 3.99 (d, *J* = 8.5 Hz, 1 H, 4-isoxazoline H), 4.41 (br. s, 1 H, CH−O), 5.28 (d, *J* = 8.5 Hz, 1 H, 5-isoxazoline H), 7.4 (m, 3 H, arom.) and 7.7 (m, 2 H, arom.). − ^{13}C NMR: δ = 38.4 (CH_2), 57.2 (C-4), 60.3 (CH−N), 78.7 (CH−O), 92.5 (C-5), 126.5, 128.8, 128.9, 130.0 (C-arom.), 156.2 (C=N). − $C_{12}H_{14}N_2O_2$ (218.2): calcd. C 66.03, H 6.47, N 12.84; found C 65.9, H 6.4, N 12.7.

Table 3. Chemical shifts and coupling constants of the adducts **5** and **6** of *N*-acyl-2-oxa-3-azanorbornenes **3**

^{1}H NMR	1-H, s	4-H, s	5-H, d	6-H, d	$J_{5,6}$	CH_2, m	*Me*$_3$-Ph, s	Me$_3$-*Ph*, s	Ph, m
5aA	4.94	5.13	4.34	5.02	8.4	2.02−2.14			7.4−7.9
5bA	4.95	5.01	4.07	5.06	8.5	2.05, 2.27	2.3	6.9	7.3−8.8
5aB (*E*)	4.79	5.34	4.30	4.93	8.5	1.94, 2.21	2.22, 2.26, 2.29	6.85	7.4−7.9
(*Z*)	5.04	4.19	3.97	5.10	8.3		2.04, 2.35, 2.45	7.22	
5bB (*E*)	4.89	5.18	4.01	4.95	7.5	3.3	3.3	6.8, 6.9	
6aA	5.02	5.12	5.19	4.24	8.2	2.08 (s)			7.4−7.8
6bA	4.73	5.19	5.20	4.01	8.1	2.18, 2.33	2.28	6.9	7.3−8.8
6aB (*E*)	5.12	5.45	5.20	4.10	7.9	2.11	2.22−2.36	6.85	7.3−7.8
(*Z*)	4.93	4.38	4.94	4.33	7.9				
6bB (*E*)	4.84	5.49	5.20	3.87	8.2	2.26	2.26	6.83, 6.9	
(*Z*)	4.58	4.40	4.92	4.10	8.2			6.89, 6.94	

^{13}C NMR	C-1	C-4	C-5	C-6
5aA	81.10	58.93	55.40	82.66
5bA	81.08	57.74	59.47	82.14
5aB (*E*)	81.04	56.52	55.97	82.59
(*Z*)	81.38	59.93	56.79	82.59
5bB (*E*)	81.02	56.28	59.95	81.90
6aA	79.98	61.95	82.68	57.33
6bA	79.66	91.94	81.76	61.29
6aB (*E*)	80.26	58.93	82.40	57.05
(*Z*)	80.26	62.22	83.11	57.41
6bB (*E*)	79.86	58.99	81.50	60.99
(*Z*)	79.86	62.25	82.23	61.31

The isomeric **8a** similarly afforded the aminol **10a** (73%), m.p. 138−139 °C. − IR: $\tilde{\nu}$ = 3360, 3290 cm^{-1} (NH_2). − ^{1}H NMR: δ = 1.7 (br. s, 3 H, NH_2 and OH), 1.85 (m, 2 H, CH_2), 3.95 (br. s, 1 H, CH−N), 4.32 (d, *J* = 8.8 Hz, 1 H, 4-isoxazoline H), 4.37 (s, 1 H, CH−O), 5.02 (d, *J* = 8.8 Hz, 1 H, 5-isoxazoline H), 7.4 (m, 3 H, arom.) and 7.8 (m, 2 H, arom.). − ^{13}C NMR: δ = 38.5 (CH_2), 59.1 (CH−N), 62.6 (C-4), 78.0 (CH−O), 91.4 (C-5), 126.9, 128.6, 128.8, 130.0 (C-arom.), 156.3 (C=N). − $C_{12}H_{14}N_2O_2$ (218.2): calcd. C 66.03, H 6.47, N 12.84; found C 66.1, H 6.6, N 12.8.

Oxidative Cleavage of the Cyclic Hydroxylamines 7a,b and 8a,b: To a stirred solution of **7a** (0.216 g, 1 mmol) and NaOAc (5 mmol) in MeOH (50 mL) was added a slight excess of *m*CPBA (0.26 g, 1.5 mmol). After keeping overnight at room temp., the solution was poured into 5% aq. Na_2SO_3 (50 mL) and extracted with AcOEt. The organic phase was washed with 5% $NaHCO_3$ and water, dried with Na_2SO_4 and concentrated at reduced pressure, leaving a 4:1 mixture (0.20 g, 86%) of the (*Z*)- and (*E*)-oximes **13a**. Crystallization from chloroform afforded the (*Z*)-oxime **13a** (41%), m.p. 170−171 °C. − IR: $\tilde{\nu}$ = 3300 cm^{-1} (OH). − ^{1}H NMR ([D$_6$]acetone): δ = 2.38 (d, *J* = 15.0 Hz, 1 H, methylene H), 2.51 (dd, *J* = 15.0 Hz, 1 H, 4.5, methylene H), 4.34 (d, *J* = 4.5 Hz, 1 H, C*H*−OH), 4.47 (br. s, 1 H, OH), 5.06 and 5.25 (d, *J* = 8.0 Hz, 2 H, 5- and 4-isoxazoline H), 7.4 (m, 3 H, arom.) and 8.0 (m, 2 H, arom.), 10.28 (s, 1 H, =N−OH). − ^{13}C NMR: δ = 36.3 (CH_2), 49.4 (C-4), 72.2 (CH−OH), 91.6 (C-5), 127.7, 127.9, 129.0, 129.6 (C-arom.), 154.9 (C=N), 157.1 (C=N−OH). − $C_{12}H_{12}N_2O_3$ (232.2): calcd. C, 62.06, H 5.21, N 12.06; found C, 62.2, H 5.3, N 11.9. − The mother liquors were concentrated, leaving a mixture of the (*E*)- and (*Z*)-oximes **13a**, which was separated by column chromatography to afford the (*E*)-oxime **13a** (15%) and the (*Z*)-oxime (20%). The (*E*)-oxime **13a** was crystallized from $CHCl_3$, colourless crystals, m.p. 130 °C. − IR: $\tilde{\nu}$ = 3340 cm^{-1} (OH). − ^{1}H NMR ([D$_6$]acetone): δ = 2.39 (dd, *J* = 17.5 Hz, 1 H, 4.5, methylene H), 3.01 (d, *J* = 17.5 Hz, 1 H, methylene H), 4.51 (d, *J* = 4.5 Hz, 1 H, C*H*−OH), 4.55 (br. s, 1 H, OH), 4.79 and 5.08 (d, *J* = 8.3 Hz, 2 H, 4- and 5-isoxazoline H), 7.4 (m, 3 H, arom.) and 7.9 (m, 2 H, arom.), 10.05 (s, 1 H, =N−OH). − ^{13}C NMR: δ = 33.1 (CH_2), 53.3 (C-4), 72.9 (CH−OH), 91.5 (C-5), 127.7, 128.0, 128.8, 129.6 (C-arom.), 156.0 (C=N), 160.0 (C=N−OH). − $C_{12}H_{12}N_2O_3$ (232.2): calcd. C 62.06, H 5.21, N 12.06; found C 62.1, H 5.3, N 12.0.

Hydroxylamine **8a** was similarly cleaved with *m*CPBA, affording a 3:1 mixture (0.21 g, 90%) of the (*E*)- and (*Z*)-oximes **14a**. The (*E*)-oxime **14a** was crystallized from ethyl acetate in colourless crystals (47%), m.p. 171−172 °C. − IR: $\tilde{\nu}$ = 3200 cm^{-1} (OH). − ^{1}H NMR ([D$_6$]acetone): δ = 2.38 (dd, *J* = 18.0 Hz, 1 H, 5.5, methylene H), 2.94 (d, *J* = 18.0 Hz, 1 H, methylene H), 4.35 (d, *J* = 9.5 Hz, 1 H, 4-isoxazoline H), 4.57 (d, *J* = 5.5 Hz, 1 H, C*H*−OH), 4.67 (br. s, 1 H, OH), 5.50 (d, *J* = 9.5 Hz, 1 H, 5-isoxazoline H), 7.5 (m, 3 H, arom.) and 7.8 (m, 2 H, arom.), 10.26 (s, 1 H, =N−OH). − ^{13}C NMR: δ = 33.7 (CH_2), 60.7 (C-4), 73.2 (CH−OH), 84.9 (C-5), 126.7, 128.7, 128.9, 129.8 (C-arom.), 156.1 (C=N), 160.7 (C=N−OH). − $C_{12}H_{12}N_2O_3$ (232.2): calcd. C 62.06, H 5.21, N 12.06; found C 62.2, H 5.4, N 12.0. − The mother liquors contained a 1:1 mixture of the (*E*)- and (*Z*)-oxime **14a**. The (*Z*)-oxime showed its characteristic ^{1}H-NM signals ([D$_6$]acetone): δ =4.39 (d, *J* = 9.5 Hz, 1 H, 4-isoxazoline H), 4.53 (d, *J* = 5.0 Hz, 1 H, *CH*−OH), 4.63 (br. s, 1 H, OH), 5.94 (d, *J* = 9.5 Hz, 1 H, 5-isoxazoline H), 10.13 (s, 1 H, =N−OH).

The mesityl hydroxylamine **7b** similarly afforded a 2:1 mixture of the (*Z*)- and (*E*)-oximes **13b** (83%), while the isomeric hydroxylamine **8b** gave a 3:1 mixture of the (*E*)- and (*Z*)-oxime **14b** (78%). The signals of the (*E*) and (*Z*) stereoisomers in the NMR spectra of the mixtures in [D$_6$]acetone correspond well to those described for the phenyl derivatives **13a** and **14a**. The crude oximes **13b** and **14b** were used as such for the hydrolysis to the ketones **17b** and **18b**.

Dehydration of the Oximes 13a and 14a: A solution of the (*Z*)-oxime **13a** (0.116 g, 0.5 mmol) and conc. HCl (0.1 mL) in MeOH (30 mL) was refluxed for 1 h. Evaporation of the solvent afforded a 3:1 mixture of the (*E*)- and (*Z*)-oximes **15a**. Separation by column chromatography afforded the major (*E*)-oxime **15a** (48%), m.p. 174−175 °C, colourless crystals from benzene. − IR: $\tilde{\nu}$ = 3290

cm^{-1} (OH). − ^1H NMR: δ = 4.73 (d, *J* = 8.2 Hz, 1 H, 4-isoxazoline H), 5.85 (dd, *J* = 8.2, 2.0 Hz, 1 H, 5-isoxazoline H), 6.60 (dd, *J* = 6.0, 2.0 Hz, 1 H, β-vinylic), 6.88 (d, *J* = 6.0 Hz, 1 H, α-vinylic), 7.22 (br. s, 1 H, OH), 7.4 (m, 3 H, arom.) and 8.9 (m, 2 H, arom.). − ^{13}C NMR: δ = 52.4 (C-4), 86.7 (C-5), 124.9, 142.1 (CH=CH), 127.8, 128.2, 128.3, 130.0 (C-arom.), 154.8 (C=N), 160.2 (C=N−OH). − $C_{12}H_{10}N_2O_2$ (214.2): calcd. C 67.28, H 4.71, N 13.08; found C 67.2, H 4.9, N 12.9. − The minor (*Z*)-oxime **15a** showed ^1H-NMR signals at δ = 5.18 (d, *J* = 8.8 Hz, 1 H, 4-isoxazoline H), 5.84 (dd, *J* = 8.8, 2.0 Hz, 1 H, 5-isoxazoline *H*), 6.38 (d, *J* = 5.8 Hz, 1 H, α-vinylic), 6.52 (dd, *J* = 5.8, 2.0 Hz, 1 H, β-vinylic). − Dehydration of the (*Z*)- and (*E*)-oximes **13a** in benzene (catalytic *p*-toluenesulfonic acid, 1 h refluxing) gave similar results.

The (*E*)-oxime **14a** was similarly dehydrated, affording a 1:1 mixture of the (*E*)- and (*Z*)-oximes **16a**. Column chromatography afforded the (*E*)-oxime **16a** (34%), m.p. 169 °C, colourless crystals from benzene. − IR: $\tilde{\nu}$ = 3200 cm^{-1} (OH). − ^1H NMR: δ = 4.84 (ddd, *J* = 8.0, 2.5, 2.2 Hz, 1 H, 4-isoxazoline H), 5.64 (d, *J* = 8.0 Hz, 1 H, 5-isoxazoline H), 6.67 (dd, *J* = 5.8, 2.5 Hz, 1 H, β-vinylic), 6.85 (dd, *J* = 5.8, 2.2 Hz, 1 H, α-vinylic), 7.38 (br. s, 1 H, OH), 7.5 (m, 3 H, arom.) and 7.8 (m, 2 H, arom.). − ^{13}C NMR: δ = 57.4 (C-4), 78.3 (C-5), 123.8, 139.6 (CH=CH), 126.5, 128.4, 128.7, 130.0 (C-arom.), 155.5 (C=N), 163.0 (C=N−OH). − $C_{12}H_{10}N_2O_2$ (214.2): calcd. C 67.28, H 4.71, N 13.08; found C 67.5, H 4.8, N 13.1. − The (*Z*)-oxime **16a** (38%) gave colourless crystals from benzene, m.p. 175−176 °C. − IR: $\tilde{\nu}$ = 3200 cm^{-1} (OH). − ^1H NMR: δ = 4.89 (ddd, *J* = 8.4, 2.5, 1.8 Hz, 1 H, 4-isoxazoline H), 6.02 (d, *J* = 8.4 Hz, 1 H, 5-isoxazoline H), 6.37 (dd, *J* = 5.8, 1.8 Hz, 1 H, α-vinylic), 6.68 (dd, *J* = 5.8, 2.5 Hz, 1 H, β-vinylic), 7.55 (br. s, 1 H, OH), 7.5 (m, 3 H, arom.) and 7.7 (m, 2 H, arom.). − ^{13}C NMR: δ = 57.6 (C-4), 82.5 (C-5), 124.1, 141.4 (CH=CH), 126.7, 128.2, 128.8, 130.3 (C-arom.), 155.0 (C=N), 161.7 (C=N−OH). − $C_{12}H_{10}N_2O_2$ (214.2): calcd. C 67.28, H 4.71, N 13.08; found C 67.1, H 4.7, N 13.2.

Ketones 17 and 18: A suspension of the (*Z*)-oxime **13a** (0.116 g, 0.5 mmol) in 5% HCl (30 mL) was refluxed for 2 h. After dilution with water and extraction with $CHCl_3$, the organic phase was dried and concentrated. Column chromatography afforded 0.072 g (71%) of the ketone **17a**, m.p. 48−49 °C. − IR: $\tilde{\nu}$ = 1712 cm^{-1} (C=O). − ^1H NMR: δ = 4.36 (d, *J* = 7.8 Hz, 1 H, 4-isoxazoline H), 5.92, (dd, *J* = 7.8, 2.0 Hz, 1 H, 5-isoxazoline H), 6.32 (d, *J* = 5.6 Hz, 1 H, α-vinylic), 7.4 (m, 3 H, arom.), 7.65 (dd, *J* = 5.6, 2.0 Hz, 1 H, β-vinylic), 7.9 (m, 2 H, arom.). − ^{13}C NMR: δ = 57.4 (C-4), 84.4 (C-5), 127.6, 127.7, 128.5, 130.4 (C-arom.), 134.1, 158.1 (CH=CH), 152.8 (C=N), 200.4 (C=O). − $C_{12}H_9NO_2$ (199.2): calcd. C, 72.35, H 4.55, N 7.03; found C, 72.3, H 4.6, N 7.0.

The (*E*)-oxime **14a** similarly afforded the ketone **18a** (68%), m.p. 115−116 °C. − IR: $\tilde{\nu}$ = 1722 cm^{-1} (C=O). − ^1H NMR: δ = 4.93 (ddd, *J* = 7.8, 2.8, 2.0 Hz, 1 H, 4-isoxazoline H), 5.08, (d, *J* = 7.8 Hz, 1 H, 5-isoxazoline H), 6.37 (dd, *J* = 5.8, 2.0 Hz, 1 H, α-vinylic), 7.5 (m, 3 H, arom.) and 7.8 (m, 2 H, arom.), 7.86 (dd, *J* = 5.8, 2.8 Hz, 1 H, β-vinylic). − ^{13}C NMR: δ = 55.2 (C-4), 81.3 (C-5), 126.6, 127.9, 129.0, (C-arom.), 134.2, 159.8 (CH=CH), 155.2 (C=N), 202.2 (C=O). − $C_{12}H_9NO_2$ (199.2): calcd. C 72.35, H 4.55, N 7.03; found C 72.4, H 4.5, N 7.0.

The mesityl ketones **17b** and **18b** were similarly obtained by hydrolyzing the crude oximes **13b** and **14b**:

Compound 17b: 75%, m.p. 95−96 °C from ethanol. − IR: $\tilde{\nu}$ = 1722 cm^{-1} (C=O). − ^1H NMR: δ = 2.14 (s, 6 H, *o*,*o*′-CH_3), 2.28 (s, 3 H, *p*-CH_3), 4.14 (d, *J* = 7.2, 2.0 Hz, 1 H, 4-isoxazoline H), 5.88 (dd, *J* = 7.2, 2.0 Hz, 1 H, 5-isoxazoline H), 6.37 (d, *J* = 5.8 Hz, 1 H, α-vinylic), 6.89 (s, 2 H, arom.), 7.71 (dd, *J* = 5.8, 2.0 Hz, 1 H, β-vinylic). − ^{13}C NMR: δ = 19.7, (*o*,*o*′-CH_3), 21.0 (*p*-CH_3), 61.0 (C-4), 83.0 (C-5), 123.8, 128.6, 136.6, 139.1 (C-arom.), 134.1, 159.0 (CH=CH), 153.7 (C=N), 200.3 (C=O). − $C_{15}H_{15}NO_2$ (241.3): calcd. C 74.66, H 6.27, N 5.81; found C 74.5, H 6.4, N 5.9.

Compound 18b: 63%, viscous oil. − IR: $\tilde{\nu}$ = 1720 cm^{-1} (C=O). − ^1H NMR: δ = 2.21 (s, 6 H, *o*,*o*′-CH_3), 2.31 (s, 3 H, *p*-CH_3), 4.71 (ddd, *J* = 8.8, 2.6, 2.2 Hz, 1 H, 4-isoxazoline H), 5.04 (d, *J* = 8.8 Hz, 1 H, 5-isoxazoline H), 6.38 (dd, *J* = 5.8, 2.2 Hz, 1 H, α-vinylic), 6.93 (s, 2 H, arom.), 7.54 (dd, *J* = 5.8, 2.6 Hz, 1 H, β-vinylic). − ^{13}C NMR: δ = 19.9, (*o*,*o*′-CH_3), 21.0 (*p*-CH_3), 59.2 (CH-C), 80.2 (CH−O), 123.8, 128.7, 136.6, 139.4 (C-arom.), 134.1, 160.1 (CH=CH), 155.7 (C=N), 202.8 (C=O). − $C_{15}H_{15}NO_2$ (241.3): calcd. C 74.66, H 6.27, N 5.81; found C 74.5, H 6.4, N 5.8.

Catalytic Hydrogenation of Ketones 17 and 18: A solution of **17a** (0.060 g, 0.3 mmol) and 10% Pd/C (0.020 g) in ethyl acetate (50 mL) absorbed 1 equiv. of hydrogen within 1 h. The catalyst was filtered off and the filtrate was concentrated under reduced pressure to give ketone **19a**, colourless crystals m.p. 95−96 °C from aqueous ethanol, identical with an authentic specimen (ref.[15] m.p. 95−96 °C). The isomeric ketone **18a** was similarly hydrogenated, affording the saturated ketone **20a**, colourless crystals m.p. 88−89 °C from cyclohexane (ref.[15] m.p. 92−93 °C).

The mesityl derivatives **17b** and **18b** were similarly hydrogenated, affording the saturated ketones **19b**, colourless crystals, m.p. 78 °C from petroleum ether (ref.[15] m.p. 78−79 °C), and **20b**, viscous oil. − IR: $\tilde{\nu}$ = 1750 cm^{-1} (C=O). − ^1H NMR: δ = 2.0−2.4 (m, 4 H, CH_2CH_2), 2.28 (s, 6 H, *o*,*o*′-CH_3), 2.32 (s, 3 H, *p*-CH_3), 4.37 (m, 1 H, 4-isoxazoline H), 4.84 (d, *J* = 9.5 Hz, 1 H, 5-isoxazoline H), 6.95 (s, 2 H, arom.). − ^{13}C NMR: δ = 20.0, (*o*,*o*′-CH_3), 20.9 (*p*-CH_3), 22.0 (CH_2), 34.3 (CH_2-CO), 52.9 (C-4), 82.3 (C-5), 123.8, 128.9, 136.8, 139.1 (C-arom.), 158.4 (C=N), 211.9 (C=O). − $C_{15}H_{17}NO_2$ (243.3): calcd. C 74.05, H 7.04, N 5.76; found C 74.2, H 7.2, N 5.8.

Cycloaddition of Mesitonitrile Oxide (2b) with 2-Cyclopenten-1-one: A solution of mesitonitrile oxide (0.8 g, 5 mmol) and excess 2-cyclopenten-1-one (4.2 mL, 50 mmol) in abs. benzene (50 mL) was kept for 1 week at room temp. The solvent was removed under vacuum and the residue chromatographed, affording ketone **19b** (0.97 g, 80%) and the isomeric compound **20b**, (0.04 g, 3%), identical with the samples obtained from hydrogenation.

Influence of Reactant Ratios in the Trapping of Nitrosocarbonyl Intermediates with Cyclopentadiene: Benzhydroximoyl chloride (0.031 g, 0.2 mmol) was added to a stirred solution of triethylamine (28 μL, 1 equiv.) and the appropriate equivs. of NMO and cyclopentadiene in CH_2Cl_2 (20 mL). In the experiments performed with MNO, the nitrile oxide (0.032 g, 0.2 mmol) was added to a stirred solution of NMO and cyclopentadiene. After keeping overnight, washing with water, drying and concentration, the ratios of the adducts **3**, **4**, **5**, and **6** were determined by NMR and are given in Table 1.

Competition Experiments: BNO (0.1 mmol) was generated in situ in, and MNO (0.1 mmol) added to, a solution of 10 equivs. of norbornene (0.094 g, 1 mmol) and the *N*-benzoyloxazanorbornenes **3A** (0.201 g, 1 mmol) in benzene (20 mL). After keeping overnight, washing with water, drying, and concentration, the ratio of the adducts was determined by NMR.

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