THE STRUCTURE AND NMR SPECTRA OF SOME DIELS-ALDER ADDUCTS OF NITROSOBENZENE, P-NITROSOTOLUENE AND 1-CHLORO-1-NITROSOCYCLOHEXANE

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Abstract - The products of the following Diels-Alder reactions have been investigated: (i) nitrosobenzene with 2-phenyl-1,3-butadiene, isoprene, piperylene, 2,3-dimethyl-1,3-butadiene, 2-methyl-3-phenyl-1,3-butadiene and 2,4-hexadiene; (ii) p-nitrosotoluene with 2,4-hexadiene; (iii) 1-chloro-1-nitrosocyclohexane with 2-methyl-3-phenyl-1,3-butadiene and 1-phenyl-1,3-pentadiene. The 4-methyl and 4-phenyl isomers are formed in relatively larger quantities in the diene reaction of isoprene and 2-phenyl-1,3-butadiene with nitrosobenzene, while the 4-methyl-5-phenyl isomer is the major product from the reaction of 2-methyl-3-phenyl-1,3-butadiene with 1-chloro-1-nitrosocyclohexane.

INTRODUCTION

Although the Diels-Alder reaction of 1,3-butadienes with 1-chloro-1-nitroso-cyclohexane or aromatic nitroso compounds has been studied extensively[1], some reactions apparently have not been investigated yet. Therefore, studies of the 1,4-cycloaddition reactions of some 1,3-butadienes with nitroso compounds have been continued. The determination of the orientation of the cycloaddition reactions of 2-phenyl-1,3-butadiene, 2-methyl-3-phenyl-1,3-butadiene and 1-phenyl-1,3-pentadiene with representative nitroso compounds is the major focus of the work reported herein.

In order to compare structural preferences in the formation of adducts from 2-phenyl-1,3-butadiene and isoprene, respectively, the addition products from isoprene and nitrosobenzene have also been prepared and examined. The adducts from 1-chloro-1-nitrosocyclohexane have been ethanolized and then isolated as hydrochlorides. The ^{1}H and ^{13}C nmr spectral data of previously reported adducts from 2,3-dimethyl-1,3-butadiene[2], piperylene[3] and 2,4-hexadiene[4] with appropriate nitroso compounds have also been examined. The regiochemistry of all prepared cycloadducts has been established by chemical and spectroscopic means. Proton nmr chemical shifts for all reported oxazines are presented in Table 1, while those for the corresponding cleavage products are presented in Table 2. Proton-proton coupling

constants for the oxazine system are displayed in Table 3. Table 4 lists the ^{13}C nmr chemical shifts for the 3-methyl-6-phenyloxazine isomers.

Table 1. Proton chemical shift of the oxazines for ca. 10% w/v solutions in $CDCl_3$ at +35°C

Compound	Chemical Shift (ppm)													Ref.
	NPh	*C(4)Ph*	*C(5)Ph*	*C(6)Ph*	C(3)H	C(4)H	C(5)H	C(6)H	C(3)Me	C(4)Me	C(5)Me	C(6)Me	C_6H_4Me	
I [b]	7.23	7.34	--	--	4.25	--	6.21	4.53	--	--	--	--	--	[a]
II [b]	7.23	--	7.34	--	4.15	6.21	--	4.61	--	--	--	--	--	[a]
III [b]	7.15	--	--	--	3.64	--	5.57	4.42	--	1.75	--	--	--	[a]
III [b]	7.20	--	--	--	3.63	--	5.63	4.63	--	1.77	--	--	--	[7]
IV [b]	7.20	--	--	--	3.72	--	--	4.35	--	--	1.68	--	--	[a]
V	7.20	--	--	--	4.06	5.83	5.83	4.38	1.07	--	--	--	--	[a]
VI	7.20	--	--	--	3.74	5.83	5.83	4.67	--	--	--	6.45	--	[a]
VII [b]	7.23	--	--	--	4.56	--	--	4.75	--	1.86	1.86	--	--	[a]
VIII [c]	7.25	--	7.36	--	3.83	--	--	4.66	--	1.75	--	--	--	[a]
IX [c,d]	--	--	7.32	--	3.54	--	--	4.40	--	1.64	--	--	--	[a]
X [c,d]	--	7.32	--	--	3.74	--	--	4.23	--	--	2.11	--	--	[a]
XI [c]	7.22	--	--	--	4.12	5.72	5.72	4.72	1.12	--	--	1.23	--	[a]
XII [e]: (A)	--	--	--	6.99	3.84	5.91	5.94	5.26	1.15	--	--	--	--	[a]
: (B)	--	--	--	7.08	3.72	5.96	6.03	5.22	1.22	--	--	--	--	[a]
XIV [c]	7.15	--	--	--	4.10	5.93	5.93	4.70	1.13	--	--	1.22	2.30	[a]

[a] - This work.
[b] - Spectra were run at 90 MHz on a Perkin-Elmer R32 Spectrometer at Stirling University, Scotland, UK.
[c] - Spectra were run at 200 MHz on a Varian XL-200 Spectrometer at Michigan Technological University, Houghton, Michigan, USA.
[d] - Spectra were run at 80 MHz on an IBM NR80 at Central Michigan University, Mt. Pleasant, Michigan, USA.
[e] - Spectra were run at 360 MHz on a Brucker WM-360 at Michigan Molecular Institute, Midland, Michigan, USA.

Table 2. Proton chemical shifts of the cleavage products for ca. 10% w/v solutions in $CDCl_3$ at +35°C

Compound	Chemical Shift (ppm)											Ref.
	NPh	*C(1)Ph*	*C(2)Ph*	*C(3)Ph*	C(1)H	C(2)H	C(3)H	C(3)Me	C(4)H	C(4)Me	OH&NH	
XV	6.90	--	--	--	4.15	5.57	--	1.74	3.68	--	3.09	[a]
XV	6.94	--	--	--	4.23	5.65	--	1.83	3.75	--	3.21	[7]
XVI	6.32	--	--	7.23	4.30	6.08	--	--	4.04	--	2.93	[a]
XVII	6.50	--	7.22	--	4.31	--	--	1.86	3.52	--	--	[a]
XVIII	--	7.35	--	--	5.49	5.66	5.44	--	3.97	1.17	3.05	[a]

[a] - This work.

Table 3. Coupling constants (H_z) in the oxazine ring measured at +35°C

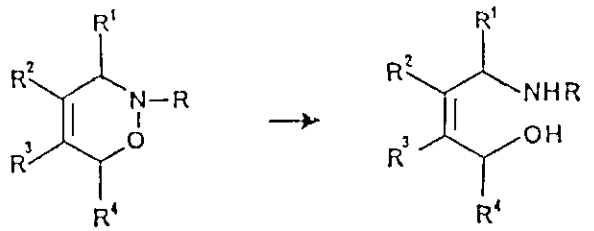
Substituents	$J_{3,4}$	$J_{3,5}$	$J_{3,6}$	$J_{4,5}$	$J_{4,6}$	$J_{5,6}$	$J_{Me,3}$	$J_{Me,6}$
2,4-diPh	—	2.3	1.6	—	—	2.9	—	—
4-Me-2-Ph	—	2.3	1.7	—	—	2.7	—	
3-Me-2-Ph	—	—	—	—	—	—	6.6	—
6-Me-2-Ph	—	—	—	—	—	—	—	6.8
4,5-diMe-2-Ph	—	—	2.0	—	—	—	—	—
3-Me-6-Ph: [A]	1.7	1.4	1.6	10.3	3.3	1.2	7.0	—
[B]	3.1	1.3	2.8	10.4	3.9	1.6	7.1	—

[A] - Isomer with chemical shift δ_A.
[B] - Isomer with chemical shift δ_B.

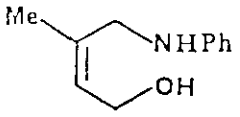
Table 4. Carbon-13 nmr parameters for the 3-Me-6-Ph oxazine isomers

Carbon	δ* ppm	$J(H-C)H_z$
Me	16.8 (s)	127
	15.0 (w)	127
C-3	51.3 (s)	136
	51.1 (w)	136
C-6	70.9 (s)	144
	71.1 (w)	144
=C-Me	130.6	
=C-Ph	138.0	
Ph(1)	140.5	160
Ph(2-6)	ca. 128.0 overlapping	

*ref. $CDCl_3$ = 77.2 ppm



I R,R^2 = Ph; R^1,R^3,R^4 = H
II R,R^3 = Ph; R^1,R^2,R^4 = H
III R = Ph; R^1,R^3,R^4 = H; R^2 = Me
IV R = Ph; R^1,R^2,R^4 = H; R^3 = Me
V R = Ph; R^1 = Me; R^2,R^3,R^4 = H
VI R = Ph; R^4 = Me; R^1,R^2,R^3 = H
VII R = Ph; R^1,R^4 = H; R^2,R^3 = Me
VIII R,R^3 = Ph; R^1,R^4 = H; R^2 = Me
IX R,R^1,R^4 = H; R^2 = Me; R^3 = Ph
X R,R^1,R^4 = H; R^2 = Ph; R^3 = Me
XI R = Ph; R^2,R^3 = H; R^1,R^4 = Me
XII R,R^2,R^3 = H; R^1 = Me; R^4 = Ph
XIII R,R^2,R^3 = H; R^1 = Ph; R^4 = Me
XIV R = C_6H_4Me; R^1,R^4 = Me; R^2,R^3 = H



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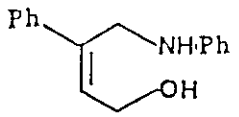

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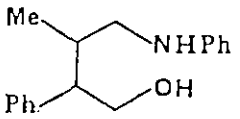
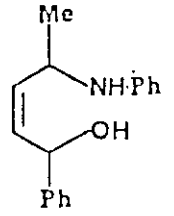


(XVII)



(XVIII)

DISCUSSION

The previously unreported reaction of 2-phenyl-1,3-butadiene with nitrosobenzene afforded a high yield (ca. 70%) of a solid which was shown to consist largely (> 95%) of the 4-phenyl isomer with the remainder being the 5-phenyl isomer. As reported earlier, the reaction of 2-phenyl-1,3-butadiene with 1-chloro-1-nitrosocyclohexane produced a mixture of the two isomeric adducts, 4-phenyl and 5-phenyl derivatives of 3,6-dihydro-1,2-oxazine in which the former predominated[5]. The fact that two reactants, diene and dienophile, each bearing a bulky substituent, produced the adduct via the more sterically hindered activated complex is an indication that the steric factor does not play a dominant role in condensations involving C-2 phenyl substituted butadienes. As in the case of the 4-phenyl adduct, either from nitrosobenzene or 1-chloro-1-nitrosocyclohexane, the regioselectivity reflects the electronic properties of reactants, the phenyl group in the diene being an electron donor. Therefore, the electronic effect is a main factor that influences the structural orientation of the reaction leading to 2,4-diphenyl-3,6-dihydro-1,2-oxazine. The structure of 3,6-dihydro-1,2-oxazines can be assigned based upon an analysis of the corresponding nmr spectra[5]. Thus, the structure (I) is indicated from the proton spectrum since the C(6)H resonance in the oxazine ring shows a stronger coupling (vicinal) to the vinyl proton compared to the coupling (allylic) of the C(3)H resonance to the vinyl proton. Decoupling of the latter gives triplets for the C(6)H and C(3)H resonances showing a homoallylic coupling of 2.3 Hz. Irradiation of the C(3)H resonance shows the C(6)H proton as a doublet with splitting of 2.9 Hz, while decoupling of the C(6)H proton gives also a doublet for the C(3)H resonance with splitting of 1.6 Hz. This is totally consistent with structure (I), and not with (II). The nmr spectrum of the cleavage product shows a triplet for the vinyl proton and a doublet for the CH_2O, while the CH_2N appears as a singlet. This locates the phenyl group in the 4 position of the oxazine ring. The spectrum thus corresponds to that expected for 2-phenyl-4-(phenylamino)-2-butenol (XVI).

The ^{1}H nmr spectrum of the adduct from isoprene with nitrosobenzene is in agreement with that reported earlier, the major component being the 4-methyl isomer (III) [6,7]. The minor isomer was detected in small amounts (IV; about 15%) only. The predominant formation of the 4-methyl isomer indicated that steric factors are not of paramount importance in this reaction. The structure of the major isomer was confirmed by decoupling experiments. Elimination of coupling from the methyl protons by irradiation showed the C(6)H resonance as a quartet. This is exactly as might be expected for collapse of a doublet of triplets in which the doublet and triplet couplings were approximately equal (2.7 Hz for the doublet and 2.3 Hz for the triplet). The C(3)H resonance, also as a quartet, similarly was consistent with a doublet coupling of about 1.7 Hz and a triplet coupling of 2.3 Hz. Thus, the structure of the major adduct was shown to be (III). The additional evidence was provided by the cleavage product, the nmr spectrum of which was consistent with the structure of 3-methyl-4-(phenylamino)-2-buten-1-ol (XV; Table 2).

The reaction of piperylene with nitrosobenzene generated a mixture of the 3-methyl- (V; ca. 53%) and the 6-methyl- (VI; ca. 47%) 3,6-dihydro-1,2-oxazines, respectively. The predominant formation of the isomer (V) was in agreement with the results previously reported[3], and confirmed that steric effects are not always a dominant factor in determining the outcome of cycloaddition reactions involving aromatic nitroso compounds.

Cycloaddition reactions of 2,3-disubstituted dienes have been little studied so far. One such compound, 2,3-dimethyl-1,3-butadiene[2,5], was found to react smoothly with nitroso compounds. However, 2,3-diphenyl-1,3-butadiene[8] does not react with aromatic nitroso compounds or 1-chloro-1-nitrosocyclohexane, most likely due to the great steric hindrance in the activated complex for cycloaddition. The reaction of 2-methyl-3-phenyl-1,3-butadiene with nitrosobenzene and 1-chloro-1-nitrosocyclohexane has been examined as part of this investigation. This diene was found to react readily with nitrosobenzene at 0°C yielding, however, 4-methyl-5-phenyl isomer (VIII) as the only product. The exclusive formation of the isomer (VIII) indicates that the orienting influence of the methyl group in the diene predominates over any orienting influence of the phenyl group. In order to determine the structure of the product, the adduct was hydrogenated using 10% Pd/C as a catalyst, and 2.0 atm. hydrogen. The reduction yielded a saturated aminoalcohol, the structure of which was established by means of two dimensional proton nmr spectroscopy. In the 2-d contour plot it was readily apparent that the methine group next to the methyl group was attached to the methylene next to the amino group rather than to the methylene adjacent to the hydroxyl group. Therefore, the aminoalcohol was demonstrated to be 3-methyl-2-phenyl-4-(phenylamino)-1-butanol (XVII), which could only have arisen from 4-methyl-5-phenyl-3,6-dihydro-1,2-oxazine.

The reaction between 2-methyl-3-phenyl-1,3-butadiene and 1-chloro-1-nitrosocyclohexane required several days at room temperature to afford an acceptable yield and produced a mixture

of two structural isomers as hydrochlorides; ca. 70% (IX) and ca. 30% (X). The predominant formation of the isomer (IX) suggests that the sterically more preferred orientation of the diene, in both reactions, either with nitrosobenzene or 1-chloro-1-nitroso-cyclohexane is that which leads to the formation of the 4-methyl-5-phenyl isomer. The ^{1}H nmr spectrum of the mixture contains well-resolved resonances for both isomers (IX and X). These isomers were identified on the basis of their ^{13}C nmr spectra which were obtained for the mixture using broad band decoupling and gated decoupling (nuclear Overhauser effect but coupled; Table 4). The methyl and methylene peaks were all pairs with the stronger of the pair having the methyl group at C-4. The assignments of peaks were based on the shifts of the oxazine carbon atoms previously reported[9], as well as on those found in available tables of ^{13}C nmr data[10]. The assignments of the methyl group at C-4 and C-5, however, were based on the fact that in the coupled spectra the strong peak assigned to C-3 and the weak peak assigned to C-6 both showed weak long range proton couplings presumably from the methyl protons.

When allowed to react with 1-chloro-1-nitrosocyclohexane as dienophile, trans-1-phenyl-1,3-pentadiene yielded preferentially the 3-methyl-6-phenyl cycloadduct (XII). The other structural isomer, 6-methyl-3-phenyl (XIII), was formed in negligible amounts (about 3%) according to the 360 MHz nmr spectrum. This implies that the activated complex leading to isomer (XII) is energetically more favored due to the stronger orienting effect of the methyl group in the diene. The 360 MHz nmr spectrum of the adduct contains two sets of resonances for each kind of oxazine proton. This could only be due to the presence of two isomeric forms in which the methyl and phenyl groups are cis and trans to each other with respect to the plane of the ring. These arise from a mixture of dienes used as starting material. Both trans, trans and cis, trans dienes are produced from dehydration of the precursor alcohol which presumably proceeds via a carbocationic intermediate. The conclusive evidence for the fact that in both isomers (δ_A & δ_B) the methyl group is attached to C-3 was provided by a 2-d COSY nmr experiment. In the 360 MHz COSY spectrum the methyl group of one isomer at δ_A=1.15 ppm had a strong cross-peak to the C-3 proton at δ_A=3.84 ppm and the latter also had cross-peaks to the vinylic protons at δ_A=5.91 ppm and δ_A=5.94 ppm, respectively. Similar connectivities were observed for the other isomer (δ_B). Thus the methyl group at δ_B=1.22 ppm also had a strong cross-peak to the C-3 at δ_B=3.72 ppm and that to vinylic protons at δ_B=5.96 ppm and δ_B=6.03 ppm respectively. The lower frequency C-5 vinylic proton had a cross-peak to the C-6 proton at δ_A=5.26 ppm and the higher to the one at δ_B=5.22 ppm. The results of decoupling experiments are in accord with the COSY results. The methyl peaks are doublets with splittings of 6.99 Hz and 7.08 Hz respectively (Table 3). Decoupling at the methyl frequency collapsed the C-3 proton signal and vice versa. Decoupling at the C-6 proton frequency had effect only on the vinylic proton resonance. Finally, to confirm these assignments, the N-O bond in the oxazine ring was

cleaved using zinc and acetic acid. The unsaturated alcohol produced (XVIII) is that which would be expected to arise from 3-methyl-6-phenyl-3,6-dihydro-1,2-oxazine. Decoupling experiments located the methyl group at C-4 and the phenyl at C-1 in the amino-alcohol structure. This was totally in agreement with the above assignments based upon spectroscopic characterization.
In conclusion, structural directivity in cycloaddition reactions of nitroso compounds depends on the steric requirements and the position of diene substituents. Steric hindrance is a more dominant factor in the reaction of 1- and 2-substituted dienes with 1-chloro-1-nitroso-cyclohexane than with nitrosobenzene. The reaction of 2,3- and 1,4-disubstituted dienes with nitrosobenzene, however, presumably proceeds via the less sterically hindered activated complex.

EXPERIMENTAL

Ir Spectra. Ir spectra were obtained using a Perkin-Elmer 720 spectrophotometer at Kumasi University, Ghana. For solid samples nujol or hexachlorobutadiene (HCB) were used as dispersants.

^{1}H Nmr Spectra. Proton nmr spectra were recorded for 10% solutions in $CDCl_3$ using either a Perkin-Elmer R32 spectrometer (90 MHz) at Stirling University (SU), Stirling, Scotland, or a Varian XL-200 spectrometer (200 MHz) at Michigan Technological University (MTU), Houghton, Michigan, USA, or an IBM NR80 spectrometer (80 MHz) at Central Michigan University (CMU), Mt. Pleasant, Michigan, USA, or a Brucker WM-360 spectrometer (360 MHz) at Michigan Molecular Instutute (MMI), Midland, Michigan, USA. Chemical shifts are reported in ppm downfield from tetramethylsilane as an internal reference. Spin-spin decoupling experiments were conducted using either a Varian XL-200 spectrometer, operating at 200 MHz (MTU) or an IBM NR80 spectrometer (CMU).

^{13}C Nmr Spectra. Spectra were recorded for ca. 20% solutions in $CDCl_3$ using an IBM NR80 spectrometer (80 MHz) at CMU.

Mass Spectra. Mass spectra were recorded using a JEOL D-100 mass spectrometer at SU.

Nitrosobenzene[11], p-nitrosotoluene, 1-chloro-1-nitrosocyclohexane[5] and the dienes, except isoprene which was purchased, were prepared by previously reported methods. Dihydro-1,2-oxazines and the corresponding cleavage products were also prepared by analogy to the methods described elsewhere[5].

2-Phenyl-1,3-butadiene. 4-Acetoxy-2-phenyl-1-butane (bp 134-136°C/14 torr) prepared from α-methylstyrene, glacial acetic acid and paraformaldehyde, was saponified with aqueous potassium hydroxide solution to afford 3-phenyl-3-butenol (bp 126-130°C/12 torr)[12]. The alcohol was dehydrated by distillation from a crystal of iodine through a helix packed column. The hydrocarbon was collected at 80-82°C/7 torr[5].

3-Methyl-2-phenyl-1,3-butadiene. 3-Methyl-2-phenyl-2-butanol (bp 88-90°C/6 torr), prepared from acetophenone and isopropyl bromide by the Grignard reaction, was converted to 3-methyl-2-phenylbut-2-ene[13] using oxalic acid as the dehydrating agent. Subsequently, 3-methyl-2-phenylbut-2-ene was treated with bromine in chloroform, the latter was removed by distillation at reduced pressure and the residue was distilled from anhydrous sodium carbonate at 100-102°C/24 torr. The distillate, 3-methyl-2-phenyl-1,3-butadiene[13], was purified by fractional distillation; bp 48-50°C/1 torr.

1-Phenyl-1,3-pentadiene. 1-Phenylpent-1-en-3-ol (bp 117-120°C/3 torr) obtained from trans-cinnamaldehyde and ethyl bromide by the Grignard reaction, when subjected to distillation at reduced pressure, yielded 1-phenyl-1,3-pentadiene, bp 92-94°C/4 torr.

2,4-Diphenyl-3,6-dihydro-1,2-oxazine (I). 2-Phenyl-1,3-butadiene (12 g; 0.090 mol) was added to nitrosobenzene (9.7 g; 0.090 mol) dissolved in benzene (50 ml). The mixture was kept at 0°C for 48 h. The solvent and unchanged nitrosobenzene were removed by distillation. The adduct, a yellowish solid, was crystallized from absolute ethanol to afford 15.4 g (70%) of the desired product, mp 62-65° (picrate, from EtOH, mp 68-70°C): ir (cm^{-1}, nujol) 3100, 2950, 2875, 1600, 1590, 1500, 1460, 1400, 900, 870, 820, 780, 760, 705.
Calcd for $C_{16}H_{15}NO$: M^+, 237.1153. Found: 237.1137.

3-Phenyl-4-(phenylamino)-2-butenol (XVI). The solution of cycloadduct (I; 2.8 g; 0.012 mol) in glacial acetic acid (25 ml) was treated with zinc dust (3.0 g). The mixture was heated for 1 h at 50°C, cooled, the zinc removed by filtration and the filtrate made alkaline. The product was extracted with chloroform and distilled at 170-176°C/2 torr (24% yield): ir (cm^{-1}, nujol) 3400, 3040, 2920, 2835, 1600, 1490, 1445, 1355, 750, 695.

4-Methyl-2-phenyl-3,6-dihydro-1,2-oxazine (III). The oxazine (bp 108-110°C/2 torr; lit.[2] bp 80-81°C/0.15 torr) was prepared in 32% yield (picrate from ETOH, mp 54-56°C) as described for I: ir (cm^{-1}, neat) 3080, 3055, 2990, 2960, 2920, 2855, 2840, 1695, 1600, 1535, 1495, 1460, 1385, 1370, 860, 800, 760, 690.
Calcd for $C_{11}H_{13}NO$: M^+, 175.0997. Found: 175.1005.

3-Methyl-4-(phenylamino)-2-butenol (XV). The compound (bp 116-120°C/2 torr) was prepared similarly to XVI: ir (cm^{-1}, neat) 3400, 3055, 2990, 2920, 1685, 1615, 1510, 1450, 1385, 1320, 752, 690.

2,5-Diphenyl-4-methyl-3,6-dihydro-1,2-oxazine (VIII). The adduct was formed from 2-methyl-3-phenyl-1,3-butadiene (9.0 g; 0.0625 mol) in diethyl ether (130 mL) and nitroso-benzene (6.7 g; 0.0625 mol). The crystals of the product appeared after 12 h at 0°C: yield 7.9 g (51%); mp; 128-130°C; ir (cm^{-1}, neat) 3120, 3080, 3050, 3020, 2970, 2950, 2910, 2860, 2840, 1600, 1570, 1540, 1500, 1460, 1400, 900, 860, 800, 770, 705.
Calcd for $C_{17}H_{17}NO$: M^+, 251.1311. Found: 251.1315.

4-Methyl-5-phenyl-3,6-dihydro-1,2-oxazine (IX) and 5-methyl-4-phenyl-3,6-dihydro-1,2-oxazine (X). (The product is a mixture of regioisomers.) The reaction of 2-methyl-3-phenyl-1,3-butadiene (16.0 g; 0.111 mol) in diethyl ether (100 ml), 1-chloro-1-nitrosocyclohexane (16.4 g; 0.111 mol), and ethanol (14 ml) proceeded at room temperature. The reaction was completed in 5 days, and the hydrochloride formed was not isolated but immediately converted into free amine, bp 124-126°C/1 torr: ir (cm^{-1}, neat) 3290, 3230, 3070, 3040, 2940, 2925, 2880, 2820, 1605, 1545, 1500, 1445, 860, 820, 770, 710.
Calcd for $C_{11}H_{13}NO$: M^+, 175.0997. Found: 175.1000.

3-Methyl-6-phenyl-3,6-dihydro-1,2-oxazine (XII). (The product is a mixture of cis and trans isomers.) The mixture of 1-phenyl-1,3-pentadiene (20.0 g; 0.138 mol) in diethyl ether (100 ml), 1-chloro-1-nitrosocyclohexane (20.5 g; 0.138 mol) and ethanol (17 ml) was kept at room temperature for 72 h (or at 0°C for 96 h) to produce the hydrochloride of (XII), which was at once converted into the amine, bp 106-108°C/1 torr: ir (cm^{-1}, neat) 3280, 3230, 3075, 3045, 2980, 2945, 2880, 1605, 1500, 1460, 900, 850, 760, 705.
Calcd for $C_{11}H_{13}NO$: M^+, 175.0997. Found: 175.0994.

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