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NMR/NOE Elucidation of the Stereostructure of Cycloadducts of Acetonitrile Oxide with Norbornane/ene-Fused Dihydro-oxazines*

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Norbornane-di-*endo*- and -di-*exo*-fused dihydro-1,3-oxazines underwent cycloaddition with *in situ* prepared acetonitrile oxide to yield tetracyclic 1,2,4-oxadiazolines. Either the C=C bond of the double dipolarophiles with the norbornene skeleton was saturated to give isoxazoline regioisomers, or a second molecule of the dipole added to the C=N bond, resulting in the formation of a bis-adduct. The structures of the products were confirmed by ^{1}H and ^{13}C NMR spectroscopy, making use of DNOE experiments.

KEY WORDS Cycloaddition of acetonitrile oxide to norbornane/ene-fused dihydro-1,3-oxazines Regioselectivity ^{1}H and ^{13}C NMR DNOE

INTRODUCTION

In previous studies[2,3] we have shown that 1,3-cycloadditions to norbornene-fused dihydro-1,3-oxazine double dipolarophiles lead to saturation of the C=C bond to give isoxazoline regioisomers, whereas the C=N bond remains unaffected. The higher reactivity of the olefinic bond is due partly to the strain in the bicycloheptane ring system, and partly to the hyperconjugative interaction between the π-electrons and the hydrogen atoms of the methylene bridge.[4] In agreement with this, the analogous cyclohexene dipolarophiles not containing a methylene bridge undergo addition to the C=N bond.[5] The formation of the C-6—O and C-7—O isoxazoline regioisomers was explained by steric effects.[2] This paper is concerned with cycloadditions with acetonitrile oxide (ANO) as a dipole instead of the previously used[2,3] benzonitrile oxide (BNO).

SYNTHESIS

The dipolarophiles **1**–**4** were synthesized from the corresponding amino alcohols with imidates.[6,7] The norbornane- or norbornene-fused dihydro-1,3-oxazines, isomeric in the positions of the hetero atoms (**5**, **6**), were prepared from bicyclo[2.2.0]heptane/ene with *p*-chloro(hydroxymethylbenzamide).[8,9]

The dipolarophiles **1**–**6** were reacted with ANO in dry diethyl ether; the reagent was prepared *in situ* from nitroethane and phenyl isocyanate in the presence of triethylamine (TEA).[10] In each case, the reaction gave a mixture of products; compounds **7**–**12** (Scheme 1) were separated from the diphenylurea side-product by column chromatography.

The norbornane-fused dihydro-oxazines (**1**, **3**, **5**) can give only C=N adducts, i.e. the 1,2,4-oxadiazolines (**7**, **9**, **11**). The cycloadditions of the double dipolarophiles **2**, **4** and **6** furnished the isoxazoline **8**, the two diastereomeric mono-adducts **10a** and **10b** and the bis-adduct **12**.

The sequence of reactivity is the same in the addition of either BNO or ANO to these dipolarophiles: the C=C bond is more reactive than the C=N bond. The difference between the 1,3-dipolar cycloadditions of these two dipoles is that with BNO the C-6—O and C-7—O isoxazoline regioisomers were obtained from the di-*endo*-fused 1,3-oxazine (**2**),[2,3] whereas with ANO the di-*exo*-dipolarophile (**4**) gave the isomers **10a** and **10b**. Although the presence of the assumed C-7—O regioisomer of **8** was detected by thin-layer chromatography (TLC), its isolation was unsuccessful.

The reaction of **6** with ANO, giving the bis-adduct as in the case of BNO,[2,3,11] is explained by the lower degree of steric hindrance of the C=N bond in **6** than in the dipolarophiles **2** and **4**.

STRUCTURE

The structures of the mono-adducts **7**–**11** and the bis-adduct **12** are confirmed by the spectral data (Tables 1 and 2). The steric structures, however, must be elucidated for each compound.

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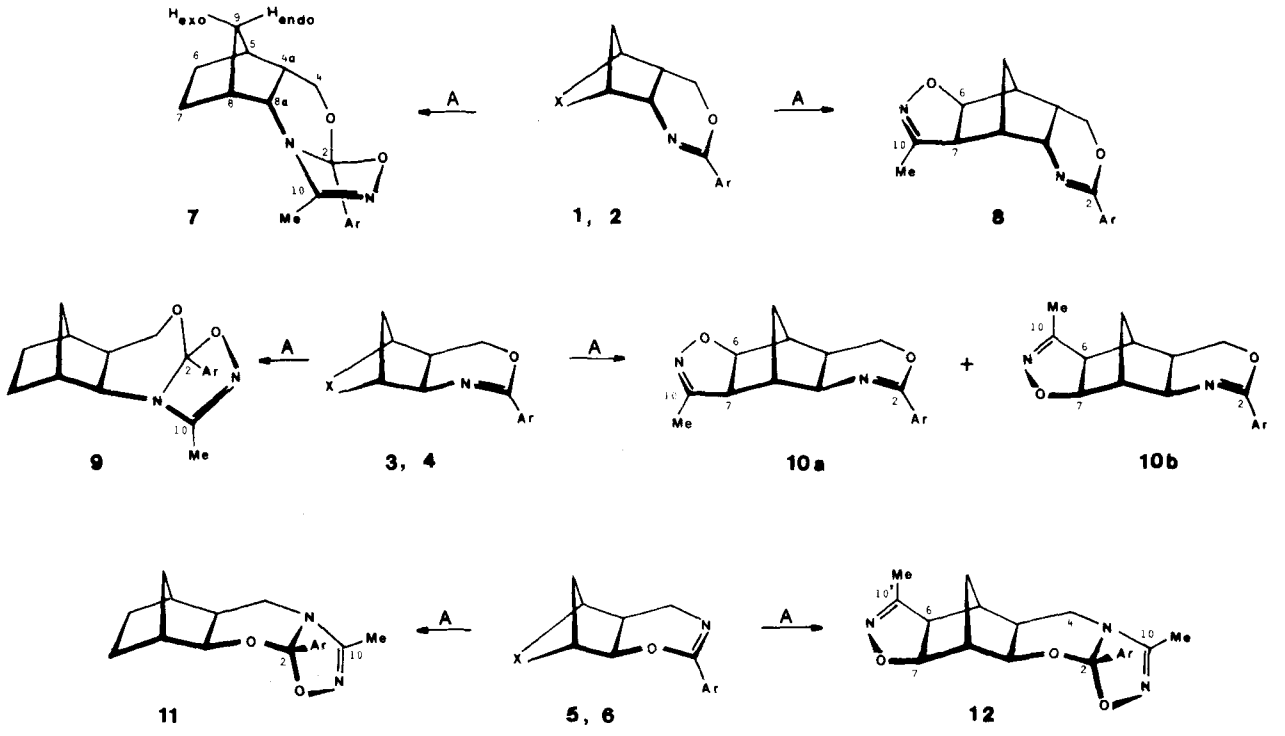

Scheme 1

The 2*S** configuration of **7** (the *endo* position of the 2-aryl group) follows unequivocally from the very similar ^{13}C and ^{1}H NMR data for the analogous BNO adduct. For instance, the chemical shifts of the skeletal carbons (except for the carbon atoms of the oxadiazoline ring and C-8a attached directly to this ring) differ by less than 0.7 ppm in the BNO and ANO adducts. The steric structure of the former was proved earlier by a

Table 1. ^{1}H NMR chemical shifts ($\delta_{TMS} = 0$ ppm) and coupling constants (Hz) of compounds 7–9, 10a, b, 11 and 12 in $CDCl_3$ solution at 250.15 MHz

Compound	CH_3 s (3H)	H-9 2 × d (2H)[a]		H-6,7 2 × m/d (2 × 2/1H)[b]		H-4a m (1H)	H-5 ~s (1H)	H-8 ~s (1H)	H-8a dd/d (1H)[c]	H-4 2 × dd (2 × 1H)[d]		ArH (position 2) 2 × m (2 × 2H)[e]	
7	2.07	~1.3[f]	~1.4[f]	1.0–1.3[f]	~1.9[g]	2.18[h]	~2.3[i]		3.88	3.90	4.06	7.33	7.47
8	1.87	1.55[i]	1.70	4.88	3.16	2.35	~2.70		4.09	~4.25		7.36	7.86
9	2.10[f]	0.80	1.82[i]	1.1	1.45	1.95[k]	2.10[f]	2.18	3.55	~3.90		7.32	7.49
10a	1.95[f]	1.35	1.48	4.54	3.16	1.95[f]	2.43	2.56	3.57	3.98	4.25	7.34	7.84
10b	1.92	1.32	1.50	3.15	4.65	2.12[l]	2.27	2.74	3.48	3.90	4.26	7.34	7.84
11	2.04	~1.15[f]	~1.9[i,m]	~1.15[f]	~1.5	~1.9[m]	~1.9[m]	2.40	3.92	3.33	2.61	7.30	7.51
12	1.89[f] 2.07[n]	1.48	~1.9[i,f]	3.05	4.48	~1.9[f]	2.15	2.78	3.98	2.71	3.41	7.33	7.49

[a] AB-type spectrum, $J = 10.0$ (**7**, **9**), 11.0 (**8**, **12**), 11.5 (**10a**, **b**).
[b] 2 × m (2 × 2H) for compounds **7**, **9** and **11**, 2 × d (2 × 1H) for compounds **8**, **10a**, **b** and **12** ($J = 8.2 \pm 0.2$), δH-6 > δH-7 for **8** and **10a**, δH-6 < δH-7 for **10b** and **12**.
[c] dd for compounds **7** ($J = 12.2$ and 3.3) and **8** ($J = 10.6$ and 4.8), d for **9** ($J = 9.2$), **10a** ($J = 8.0$), **10b** ($J = 7.6$), **11** and **12** ($J = 6.2$).
[d] AB part of an ABX spin system. The close 8 lines are partly coalesced for compounds **8** and **9** (A part of a spin system near to the limiting case A_2X). ^{2}J(H-4eq,H-4ax) = 12.7 (**7**), 11.4 (**10a**, **b**), 14.4 (**11**, **12**), ^{3}J(H-4eq,4a) < 1 (**7**), 4.8 (**10a**), 5.6 (**10b**), 7.5 (**11**, **12**), ^{3}J(H-4ax, H-4a) = 5.0 (**7**), 6.3 (**10a**), 6.7 (**10b**), 12.1 (**11**, **12**).
[e] AA'BB'-type spectrum, J(A,B): 8.6 ± 0.1.
[f,m] Overlapping signals, intensity 5H (**7**, **12**), 4H (**9**, **10a**), 3H (**11**).
[g] Intensity 1 H.
[h] dt.
[i] Coalesced ms of close lines (2H).
[j] H-9(*endo*).
[k] ~d.
[l] qa.
[n] Oxadiazoline ring.

Table 2. ^{13}C NMR chemical shifts (δ_{TMS} = 0 ppm) of compounds 7–9, 10a, b, 11 and 12 in $CDCl_3$ solution[a] at 20.15 MHz[b]

Compound	C-2	C-4	C-4a	C-5	C-6	C-7	C-8	C-8a	C-9	CH_3	C-10[c]	C-1'[d]	C-2',3',5',6'[d]		C-4'[d]
7	114.3	59.9	35.6	41.5	24.3	23.0	43.0	55.3	38.9	10.9	155.5	140.3	126.2	128.3	134.3
8[e]	155.4[f]	65.1	36.0	44.1	82.2	49.0	53.2[g]	54.3[g]	33.0	11.7	157.2[f]	137.1	128.5	128.6	131.8
9	114.6	64.3	42.5[f]	42.7[f]	30.1[g]	29.5[g]	44.6[f]	58.2	37.0	11.5	155.8	141.6	128.6	129.7	134.9
10a	157.0	65.9	36.2	46.2[f]	85.6	58.9[g]	47.2[f]	56.1[g]	27.7	11.6	154.5	136.8	128.2	128.4	131.9
10b	157.2	66.1	40.9[f]	51.6[g]	61.3	84.8	42.3[f]	52.8[g]	29.0	11.7	154.2	137.0	128.4	128.6	132.2
11[e]	113.8	40.0	38.1	41.8	29.3	23.3	44.9	74.5	38.2	10.3	153.7	138.5	127.4	128.1	134.7
12[e]	114.1	39.1	39.6	49.9	61.3	81.8	43.5	69.2	27.7	10.4[h] 11.5	153.6[h] 154.1	137.9	127.3	128.4	135.2

[a] The solvent was DMSO-d_6 for compound **9**.
[b] Measuring frequency was 62.89 MHz for compound **7**.
[c] The sp^2 carbon in the five-membered hetero ring.
[d] *p*-Chlorophenyl group.
[e] Assignments were proved by DEPT measurements.
[f,g] Interchangeable assignments.
[h] Oxadiazoline ring.

detailed analysis of the ^1H and ^{13}C NMR spectra, involving a comparison of the data for the starting compound **1** and the diphenylnitrilimine (DPNI) and BNO adducts, and also by DNOE (differential nuclear Overhauser effect) measurements.[3] The similar magnitudes of the H-4,4a and H-4',4a couplings (5.0 and <1 Hz, respectively) confirm the analogous chair-like conformation of the oxazine ring in both the ANO and BNO adducts.

The saturation of the C=C bond and the unchanged C=N bond in **8** are obviously shown by the chemical shifts of the signals of H-6,7 and C-2,6,7. The di-*exo*-annelation of the isoxazoline ring follows from the doublet splitting of the H-6,7 signals.[12] It still remained to be elucidated whether the oxygen in the isoxazoline ring is attached to C-6 or C-7, i.e. which of the two possible regio-isomers is formed. For the BNO adducts a decision was easier, as both isomers were available and their spectral data could be compared. In the present instance, **8** was subjected to DNOE measurement. When the downfield doublet at 4.88 ppm (due to either H-6 or H-7 adjacent to the oxygen) was saturated, the signal intensity of the 4-methylene hydrogens of the oxazine ring increased, whereas irradiation of the doublet (at 3.16 ppm) of the other isoxazoline hydrogen atom did not produce such a change. Consequently, the bonding of the oxygen to C-6, i.e. structure **8**, is supported. The DNOE measurements also revealed that the upfield doublet of the 9-methylene signals was due to the *endo*-hydrogen.

In the analogues of **9** formed by diphenylnitrilimine (DPNI) and BNO addition, the H-9 *endo* chemical shifts (2.20 and 1.90 ppm, respectively) are markedly different.[3] This fact and the DNOE spectra unequivocally indicate the *exo* position of the five-membered hetero ring and, consequently, the *endo* position of the *p*-chlorophenyl group. Since the H-9 chemical shifts in **9** hardly differ (by 0.04 and 0.08 ppm) from those in the phenyl analogue,[3] a similar steric structure (i.e. the 2*S** configuration) is evident. This is confirmed by the similar extent and the same direction of the chemical shifts of the skeletal carbon atoms; the C-4,4a,5,6,7,9 shifts are increased by only 0.5–2.0 ppm, but this is due mainly to the solvent effect, as the data for **9** were recorded in DMSO-d_6, and those for the phenyl analogue in $CDCl_3$. The difference in substitution gives rise to shifts of 0.7–2.4 ppm, but in the opposite direction, in the signals of C-2,8,8a,10.

The addition of ANO to the starting compound **4** gave two regioisomers (**10a**, **b**) which could be separated. As the spectra of the pure isomers could therefore be compared in this case, the determination of their structures seemed to be simpler and more reliable.

The saturation of the C=C bond and the presence of the unaltered C=N bond in both compounds (i.e. the formation of mono-adducts), and also the di-*exo*-annelation of the isoxazoline ring to the norbornene skeleton (as in **8**), was concluded from the H-6,7 and C-2,6,7 chemical shifts and from the doublet splitting of the former two signals.

In the previously studied BNO additions, two regioisomers were formed from the compound containing a di-*endo*-annelated oxazine ring (**2**), and these isomers could be readily differentiated on the basis of the large variance (0.6 and 1.3 ppm) between the chemical shift differences $\delta\Delta$H-6,7.[3] However, these two values show only a small difference (1.38 and 1.50 ppm) for the isomers **10a** and **b**.

When the chemical shifts of the signals of the skeletal carbons are compared with those of the phenyl analogues, the total difference for **10a** is about 8 ppm, whereas for **10b** it is 32 ppm. This suggests that the phenyl-substituted compound and **10a** have similar structures, i.e. the formation of the C-6—O regioisomer can be inferred. However, as some assignments are uncertain (the shifts of two pairs of lines may be reversed in two cases), and the substituent effects can only by estimated approximately, it was necessary to support this assumption directly by DNOE measurements.

When the upfield signal of the pair H-5,8 in **10a** was irradiated at 2.43 ppm, DNOE signals were obtained not only for the doublet (at 4.54 ppm) of the hydrogen adjacent to the isoxazoline oxygen and for the H-4eq double doublet (3.98 ppm), but also for the quartet-like signal of H-4a. This affords evidence that the irradiated signal is due to H-5, and consequently the doublet at 4.54 ppm is (as expected) the signal of the C-6—H atom.

In the reverse DNOE experiment, the downfield-positioned H-8 signal was irradiated. In addition to the H-8a and methyl signals, a response was obtained from the doublet at 3.16 ppm due to the other hydrogen in the isoxazoline ring; hence H-7 is responsible for the latter signal.

Confirmation of the correct assignment is given by the fact that the DNOE spectrum obtained on irradiation of the H-6 doublet shows the H-7 doublet (3.16 ppm), the H-5 singlet (2.43 ppm) and the H-4a quartet.

When the doublet at 4.65 ppm due to the methine group adjacent to the oxygen in **10b** is saturated, intensity increases are observed in its doublet pair at 3.15 ppm, in the signal of the H-8a doublet (3.48 ppm) and in the downfield signal at 2.74 ppm of the singlet-like signals due to the pair H-5,8. The bonding between C-7 and the oxygen is therefore proved by the response of the H-8a doublet.

In agreement with this, saturation of the H-5 singlet at 2.27 ppm results in an increased intensity of the H-6 (3.15 ppm), H-4eq (3.90 ppm) and methyl signals; the very close-lying H-4a signal is also saturated in this experiment.

The carbon chemical shifts in **11** (with the exception of those of C-2 and C-4, which are close to the different substituents) also match (within 0.4 ppm) the shifts found for the 2,10-diaryl analogue, the structure of which has been proved.[3] The shifts of the H-8a, H-9(*endo*) and H-4'ax, H-4eq ^{1}H NMR signals, which are the most sensitive indicators of the steric structure, are very similar. In addition, the vicinal couplings of the latter hydrogens with H-4a hardly differ; consequently, the analogous steric structure, including the conformation of the oxazine ring, is certain.

In a similar manner as with BNO addition, the stereohomogeneous bis-adduct was formed with ANO only from **6**. Since the two fused hetero rings in the product (**12**), either together or alone, influence the shielding of all the hydrogen and carbon atoms of the skeleton, the steric structure can be determined unambiguously only by NOE measurements.

The singlet-like signal at 2.78 ppm, with a striking downfield shift and overlapped by a line of the H-4'ax double doublet, is due to H-8; this is clearly shown by the appearance of the intense H-8a doublet (3.98 ppm) in the DNOE spectrum recorded after saturation of the H-8 signal. Since, at the same time, the downfield signal of the H-6,7 pair, i.e. the doublet of the hydrogen geminal to the oxygen, also appears (at 4.48 ppm) in the DNOE spectrum, it is evident that the compound contains the isoxazoline oxygen bonded to C-7, in an analogous manner to that in **10b**. This is supported by the large downfield shift of the H-8 signal, similar only to the case in **10b**, and by the corresponding C-5,6,7,8 chemical shifts, the average difference being less than 2 ppm.

Irradiation of the aromatic hydrogens did not cause an increase in intensity of the H-4a,8a signals, and no other changes were observed; this is indicative of the *exo* position of the aryl group, i.e. the fused hetero rings are in the same mutual steric position as proved for **11**. In accordance with this, the shifts of the C-2 and C-4 signals differ by only 0.3 ppm from those measured for **11**.

Of the two downfield doublets, the correct assignment of that at 3.98 ppm to H-8a is indicated by the DNOE spectrum obtained on saturation of this signal; this spectrum exhibits the H-4a quartet at about 1.95 ppm, which is overlapped in the normal spectrum by the singlet of the methyl group attached to the isoxazoline ring; of course, the H-7 doublet and H-5 singlet are also present.

On the other hand, saturation of the H-7 doublet at 4.48 ppm brings about a response in its counterpart at 3.05 ppm, i.e. the H-6 doublet, and naturally also in the H-5 and H-8a signals.

The assignments of the two methyl signals were decided by irradiation of these lines. On saturation of the upfield signal the H-9 doublet at 1.48 ppm became more intense, indicating that this is the signal of the *exo* 9-methylene hydrogen, and that the corresponding methyl group is attached to the isoxazoline ring. A response was also observed for the H-6 doublet and H-5 singlet. Irradiation of the downfield methyl signal, which must therefore be due to the substituent on the oxadiazoline ring, resulted (as expected) in increased intensity for the signals of the *ortho*-aryl hydrogens and the double doublet of H-4eq.

EXPERIMENTAL

The NMR spectra were recorded in $CDCl_3$ solution in a 5-mm (^{1}H, ^{13}C) or 10-mm (^{13}C) tube at room temperature on a Bruker WM-250 (^{1}H, ^{13}C) or WP 80 SY (^{13}C) Fourier transform spectrometer controlled by an Aspect 2000 computer at 250.13 MHz (^{1}H) and 62.89 or 20.14 MHz (^{13}C), with the deuterium signal of the solvent as the lock, and TMS as internal standard. The most important measuring parameters were as follows: for ^{1}H, spectral width 5 kHz, pulse width 1 μs (*ca.* 20° flip angle), acquisition time 1.64 s, number of scans 16 or 32, computer memory 16K and Lorentzian exponential multiplication for signal-to-noise enhancement (line width 0.7 Hz) was applied; for ^{13}C, spectral width 15 or 5 kHz, pulse width 7.5 or 3.5 μs (*ca.* 30° flip angle), acquisition time 0.5 or 1.64 s, number of scans 1–21K, computer memory 32 or 16K, and complete proton noise decoupling (*ca.* 3 or *ca.* 1.5 W) and Lorentzian exponential multiplication for signal-to-noise enhancement were used (line width 1.0 or 2.0 Hz).

The DEPT[13] spectrum was recorded in a standard manner,[14] using only the $\theta = 135°$ pulse to separate the CH/CH_3 and CH_2 lines phased 'up and down,' respectively. Typical acquisition data were number of scans 128–12K, relaxation delay for hydrogens 3 s and 90° pulse widths 10.8 and 22.8 μs for ^{13}C and ^{1}H, respectively. The estimated value for J(CH) resulted in a 3.7-ms delay for polarization.

The DNOEMULT.AU standard Bruker microprogram to generate NOE was used with a selective pre-irradiation time of 5 μs and a decoupling power (CW mode) of *ca.* 30–40 mW; number of scans 64–256, dummy scans 4–8, pulse width 5.0 μs (90°) and 16K data points for a *ca.* 2 kHz spectral width. A line broadening of 1.0 Hz was applied to diminish residual dispersion signals in the difference spectra.

Table 3. Physical and analytical data for compounds 7–12

Compound	M.p. (°C)	Yield[a] (%)	Formula	Required/found (%) C	H	N
7	184–186	41	$C_{17}H_{19}N_2ClO_2$	64.05/64.14	6.00/5.90	8.79/8.87
8	186–189	29	$C_{17}H_{17}N_2ClO_2$	64.46/64.20	5.41/5.25	8.84/8.76
9	132–134	40	$C_{17}H_{19}N_2ClO_2$	64.05/63.92	6.00/6.17	8.79/8.98
10a	114–116	16	$C_{17}H_{17}N_2ClO_2$	64.46/64.60	5.41/5.57	8.84/9.04
10b	159–162	19	$C_{17}H_{17}N_2ClO_2$	64.46/64.64	5.41/5.60	8.84/8.93
11	163–165	42	$C_{17}H_{19}N_2ClO_2$	64.05/63.90	6.00/5.92	8.79/8.70
12	233–235	38	$C_{19}H_{20}N_3ClO_3$	61.04/60.89	5.39/5.11	11.24/11.10

[a] Data refer to the pure compounds.

Preparation of 10a*t*/*c*-*p*-chlorophenyl-5,8-methano-3-methyl-4a*r*,5*t*/*c*,6,7,8*t*/*c*,8a*c*-hexahydro-9*H*-[1,2,4]oxadiazolo[4,5-*a*]benzoxazine (7/9), 6-*p*-chlorophenyl-4,9-methano-3-methyl-3a*r*,4*c*,4a*t*/*c*,8a*t*/*c*,9*c*,9a*c*-hexahydro-8*H*-[1,2]isoxazolo[5,4-*g*][3,1]benzoxazine (8a/10a), 7-*p*-chlorophenyl-4,9-methano-3-methyl-3a*r*,4*c*,4a*c*,8a*c*,9*c*,9a*c*-hexahydro-5*H*-[1,2]isoxazolo[4,5-*g*]benzoxazine (10b), 10a*t*-*p*-chlorophenyl-6,9-methano-3-methyl-5a*r*,6*c*,7,8,9*c*,9a*c*-hexahydro-5*H*-[1,2,4]oxadiazolo[5,4-*b*][1,3]benzoxazine (11) and 9a*t*-*p*-chlorophenyl-4,11-methano-7-methyl-3a*r*,4*c*,4a*c*,10a*c*,11*c*,11a*c*-hexahydro-5*H*[1,2]isoxazolo[4,5-*g*][1,3]benzoxazino-[3,2-*d*][1,2,4]oxadiazole (12)

The numbering of the chemical names according to IUPAC nomenclature is not identical with that used in the text, tables and Scheme 1, in order to facilitate the comparison of spectroscopically analogous data.

To a dry ethereal solution (50 ml) of **1–6** (1.3 g; 5 mmol) were added phenylisocyanate (1.2 g; 0.01 mol) and trimethylamine (TEA) (0.5 g; 5 mmol), and then a mixture of ethyl nitrite (0.4 g; 5 mmol) and TEA (0.2 g; 2 mmol) in dry diethyl ether (50 ml) dropwise, over 1 h, with stirring. Stirring was continued for 6 h and the solid was then removed by filtration. After evaporation of the solvent from the filtrate, the residue was transferred to a silica gel column and eluted first with benzene, then with ethyl acetate. The residue of the latter eluate was crystallized from ethyl acetate. The separated crystals were collected by filtration and the filtrate was chromatographed again through an alumina (neutral, Woelm) column. The ethyl acetate eluate (of which the first part contained **10a** and the second part **10b**; TLC control) was evaporated and crystallized from ethyl acetate–light petroleum. Data on the colourless crystalline substances **7–12** are listed in Table 3.

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