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Preparation and Reactivity of 2-Aza-1,3-butadienes: A Diels-Alder Route to 5,6-Dihydro-2*H*-1,3-oxazine Derivatives

*José Barluenga**[a], *Jesús Joglar*[a], *Santos Fustero*[a], *Vicente Gotor*[a], *Carl Krüger**[b], and *Maria J. Romão**[b]

Departamento de Química Orgánica, Facultad de Química, Universidad de Oviedo[a], Oviedo, Spain, and

Max-Planck-Institut für Kohlenforschung[b], Kaiser-Wilhelm-Platz 1, D-4330 Mülheim an der Ruhr, West Germany

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2-Aza-1,3-butadiene derivatives **2** are synthesized by dimerization of imines **1**. These azadienes are precursors of 5,6-dihydro-2*H*-1,3-oxazine derivatives **4** and **5** by means of a [4 + 2]cycloaddition reaction with aldehydes.

Darstellung und Reaktivität von 2-Aza-1,3-butadienen: Ein Diels-Alder-Weg zu 5,6-Dihydro-2*H*-1,3-oxazin-Derivaten

Die 2-Aza-1,3-butadien-Derivate **2** wurden durch Dimerisierung von Iminen **1** synthetisiert. Durch Reaktion von **2** mit Aldehyden entstehen durch [4 + 2]-Cycloaddition die 5,6-Dihydro-2*H*-1,3-oxazin-Derivate **4** und **5**.

The growing interest of 2-aza-1,3-butadienes as reactants in organic synthesis, especially for the preparation of nitrogen-containing heterocycles[1], prompted us to investigate the reactivity of this system.

Recently different methods for the synthesis of 2-aza-1,3-butadienes[2], most of them functionalized[1], have been described. However, little is known about the reactivity of these systems.

Results and Discussion

I. Synthesis and Characterization of 2-Aza-1,3-butadienes 2

In the course of our study of azine-imine exchange reactions[3] it was observed that variable amounts of 2-aza-1,3-butadienes **2** were produced as by-products in the preparation of the starting imines[4]. The interest in these systems prompted us to optimize a method to obtain compounds **2** in high yield. Thus, compounds **2** are synthesized in nearly quantitative yields by refluxing a THF solution of imine **1** in presence of catalytic amounts of trifluoroacetic acid for two hours, followed by evaporation of solvents and high vacuum distillation.

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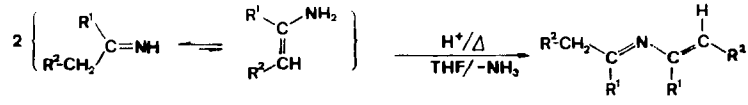
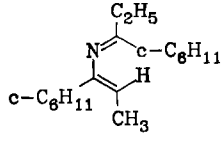


1a-f 2a-f

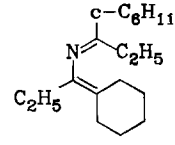
	a	b	c	d	e	f
R^1	C_6H_5	4-CH_3-C_6H_4	C_6H_5	c-C_6H_{11}	*n*-C_3H_7	c-C_6H_{11}
R^2	CH_3	CH_3	C_2H_5	C_6H_5	C_2H_5	CH_3

H_3O^+ / Δ, $-NH_3$ → $R^1(C{=}O)CH_2R^2$

Apart compound **2f**, all the 2-azadienes **2** (entries **a**–**e**) were isolated as a sole isomer. In case of diene **2f** (R^1 = c-C_6H_{11}, R^2 = CH_3) a ca. 1:1 mixture of **2f** and **2f'** was obtained:



2f



2f'

The structure of **2** was ascertained by spectral data (IR, ^{1}H NMR, ^{13}C NMR and MS) as well as by chemical methods; for instance, the hydrolysis of **2** with 6 N H_2SO_4 in THF under reflux affords the corresponding ketone as the sole organic product.

II. Synthesis of 5,6-Dihydro-2*H*-1,3-oxazine Derivatives 4

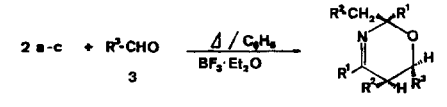
The few available studies on 2-aza-1,3-butadienes have indeed shown that they are able to undergo [4 + 2]cycloadditions with conventional electron-poor dienophiles. However, those azadienes have to bear electron-donating substituents, e.g. alkoxy or amino groups[1]. On the other hand, the reaction of simple 2-aza-1,3-butadienes with dienophiles containing electron-withdrawing groups, such as DMAD, TCNE or others, does not lead to the Diels-Alder cycloadduct[2b,2e].

In this paper the [4 + 2]cycloaddition of 2-azadienes of type **2** with aldehydes **3** is first reported[5]. Thus, heating of compounds **2a**–**c** at 60 °C with **3** and catalytic amounts of $BF_3 \cdot Et_2O$ (ratio **2**:**3**:cat. = 1.0:1.1:0.1) in benzene for 1–2 days resulted in the formation of *cis*-5,6-dihydro-2*H*-1,3-oxazine derivatives **4**[6] in high yields.

In some instances (entries **4a**–**d**) the reaction also works well in the absence of Lewis acid catalyst. For instance, the reaction of **2a** with benzaldehyde at 60 °C during 90 hours in different solvents (THF, $HCCl_3$, CCl_4, C_6H_6) leads to the formation of **4a** as well. The reaction was monitored by ^{1}H NMR and found that no appreciable changes on the reaction rate took place regardless of the solvent used.

The structure and stereochemistry of **4** was ascertained on the basis of spectral data. The ^{1}H NMR spectra of **4a**, for example, shows characteristic signals at

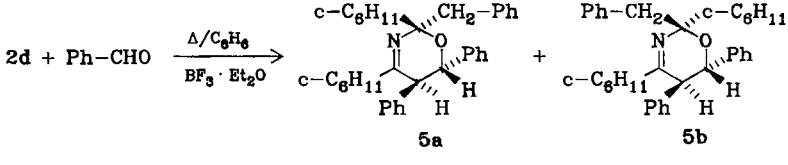
δ 4.7 (6-H, d, J = 3.1 Hz) and 3.0 (5-H, qd, J_1 = 6.3 Hz, J_2 = 3.1 Hz). The values of chemical shifts, the multiplicity of the signals and the values of the coupling constants corroborate the C-5 and C-6 stereochemical assignment.



4	R^1	R^2	R^3	yield (%)
a	C_6H_5	CH_3	C_6H_5	95
b	C_6H_5	CH_3	$4-Cl-C_6H_4$	85
c	C_6H_5	CH_3	$4-NO_2-C_6H_4$	90
d	C_6H_5	CH_3		89
e [7]	C_6H_5	CH_3	$4-CH_3-C_6H_4$	75
f	C_6H_5	CH_3		76
g	C_6H_5	CH_3		81
h	C_6H_5	CH_3	$n-C_4H_9$	70
i [7]	C_6H_5	CH_3	$i-C_3H_7$	75
j [8]	C_6H_5	CH_3	$C_2H_5CH(Cl)$	78
k [8]	C_6H_5	CH_3	$CH_3CH(C_6H_5)$	78
l	C_6H_5	C_2H_5	C_6H_5	85
m	$4-CH_3-C_6H_4$	CH_3	C_6H_5	80
n	$4-CH_3-C_6H_4$	CH_3	$4-CH_3-C_6H_4$	75
o	$4-CH_3-C_6H_4$	CH_3	$4-CH_3O-C_6H_4$	72

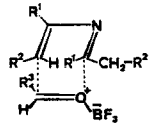
An X-ray crystallographic analysis definitively established the **4a** structure (See X-ray diffraction analysis of **4a**).

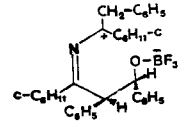
On the contrary, the reaction of **2d** with benzaldehyde and $BF_3 \cdot Et_2O$ in the above conditions[9] leads to a diastereoisomeric mixture of *trans* C-5-C-6 oxazines



5a and **5b** (yield 86%). 300 MHz ^{1}H NMR of compound **5** shows a 2.5/1 ratio of **5a**/**5b**. Further, protons at C-5 and C-6 appear in both isomers as doublets with a coupling constant of 9.7 Hz thus confirming the proposal stereochemistry.

The formation of heterocycles **4** may be rationalized in terms of a [4 + 2]cycloaddition reaction with a very high *endo* selectivity[10]. A different pathway is followed in the formation of **5**. This process, which takes place with high *trans* stereospecificity, can be regarded as a two-step cycloaddition through a zwitterionic species[11]:





III. X-Ray Diffraction Analysis of 4a

A list of final atomic coordinates with standard deviations and final thermal parameters is given in Table 1. In Table 2 relevant bond distances and bond angles of **4a** are listed. Fig. 1 shows a molecular plot of the compound **4a**.

Table 1. Final atomic coordinates with their standard deviations and final thermal parameters

ATOM	X	Y	Z	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
C1	0.1806(1)	0.5119(1)	0.8913(1)	0.034	0.037	0.042	-0.012	0.012	0.000
C2	0.2564(1)	0.4334(1)	1.0279(1)	0.046	0.039	0.036	-0.013	0.013	0.000
C3	0.2126(1)	0.3098(1)	0.9808(1)	0.037	0.039	0.038	-0.009	0.013	0.003
C4	0.1379(1)	0.3366(1)	0.7272(1)	0.040	0.036	0.037	-0.012	0.008	0.003
C5	0.2073(2)	0.2957(1)	0.6143(1)	0.051	0.048	0.042	-0.019	0.017	-0.001
C6	0.3616(2)	0.3211(2)	0.6647(2)	0.054	0.067	0.065	-0.023	0.029	-0.005
C7	0.4297(2)	0.4170(2)	1.0991(2)	0.052	0.061	0.053	-0.027	-0.005	0.014
C8	0.1747(1)	0.6474(1)	0.9107(1)	0.037	0.037	0.046	-0.011	0.014	0.001
C9	0.1558(2)	0.7093(1)	0.7933(2)	0.054	0.043	0.050	-0.013	0.022	0.003
C10	0.1501(2)	0.8345(1)	0.8075(2)	0.078	0.045	0.069	-0.019	0.032	0.006
C11	0.1628(2)	0.9001(1)	0.9387(2)	0.084	0.039	0.084	-0.023	0.035	-0.003
C12	0.1824(2)	0.8407(1)	1.0567(2)	0.081	0.048	0.064	-0.027	0.032	-0.015
C13	0.1888(2)	0.7145(1)	1.0441(2)	0.063	0.044	0.051	-0.020	0.023	-0.004
C14	0.2981(1)	0.2125(1)	1.0971(1)	0.041	0.038	0.041	-0.012	0.012	0.002
C15	0.2386(2)	0.2060(1)	1.1953(2)	0.049	0.053	0.048	-0.013	0.019	0.005
C16	0.3131(2)	0.1142(1)	1.2995(2)	0.074	0.059	0.048	-0.021	0.025	0.007
C17	0.4482(2)	0.0292(1)	1.3075(2)	0.080	0.045	0.044	-0.009	0.014	0.009
C18	0.5080(2)	0.0361(1)	1.2125(2)	0.062	0.051	0.047	0.005	0.015	0.008
C19	0.4350(2)	0.1275(1)	1.1077(2)	0.052	0.048	0.051	-0.003	0.019	0.007
C20	-0.0197(1)	0.3116(1)	0.6603(1)	0.043	0.049	0.035	-0.017	0.011	0.001
C21	-0.0279(2)	0.1887(1)	0.6478(2)	0.061	0.052	0.061	-0.028	0.017	-0.001
C22	-0.1679(3)	0.1619(2)	0.5781(2)	0.078	0.078	0.076	-0.049	0.029	-0.010
C23	-0.3016(2)	0.2566(2)	0.5217(2)	0.057	0.116	0.065	-0.048	0.021	-0.009
C24	-0.2943(2)	0.3766(2)	0.5350(2)	0.042	0.094	0.074	-0.017	0.014	0.008
C25	-0.1533(2)	0.4055(1)	0.6055(2)	0.044	0.058	0.057	-0.012	0.015	0.007
N	0.1227(1)	0.4692(1)	0.7590(1)	0.041	0.038	0.040	-0.012	0.010	0.003
O	0.2395(1)	0.2602(1)	0.8523(1)	0.042	0.038	0.037	-0.008	0.011	0.003

Due to its partial saturation, the oxazine ring is puckered into a half-chair conformation, with four ring atoms – C2, C1, N, C4 – defining a plane (±0.024 Å) from which the two remaining atoms, O and C3, are 0.293 Å and 0.478 Å, respectively, displaced to opposite sides of the plane. This type of conformation is common to other heterocyclic systems (1,2-oxazine[12], dihydrouracil[13]).

Table 2. Relevant bond distances (Å) and bond angles (°)

C1–C2	1.525 (2)	O–C3	1.430 (2)	C4–C20	1.534 (3)
C1–N	1.274 (2)	C3–C2	1.532 (2)	C4–C5	1.530 (3)
N–C4	1.452 (2)	C2–C7	1.537 (3)	C5–C6	1.522 (3)
C4–O	1.433 (2)	C1–C8	1.497 (2)	C3–C14	1.508 (2)
C4–N–C1	121.1 (1)	C1–C2–C7	110.0 (2)		
N–C1–C2	124.1 (2)	O–C3–C14	108.6 (1)		
C1–C2–C3	107.9 (1)	C2–C3–C14	114.8 (1)		
C2–C3–O	108.3 (1)	O–C4–C20	109.9 (1)		
C3–O–C4	111.6 (1)	O–C4–C5	105.7 (1)		
O–C4–N	114.3 (1)	N–C4–C20	110.0 (1)		
C8–C1–N	116.8 (2)	N–C4–C5	107.8 (1)		
C8–C1–C2	119.1 (2)	C5–C4–C20	109.0 (1)		
C3–C2–C7	113.5 (2)				

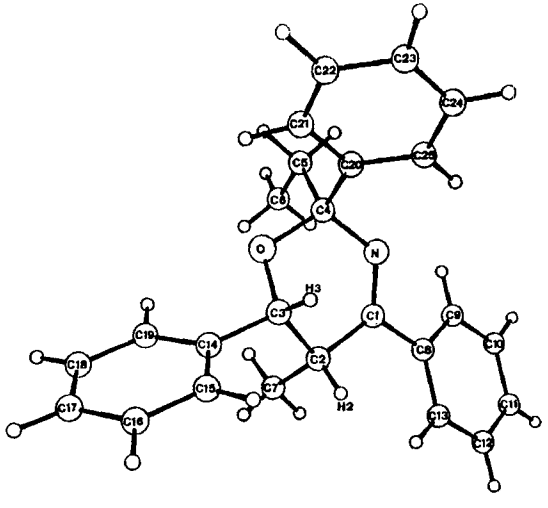


Fig. 1. Molecular plot of **4a**

The Csp^3-Csp^3 bond distances (varying from 1.522 to 1.537 Å) are in good agreement with the normal value. The smaller value observed for C1–C8 (1.497 (2) Å), compared to C1–C2 (1.525 (2) Å), is due to the conjugation between the

phenyl group bonded at C8 and the oxazine ring, despite a torsional angle N–C1–C8–C9 of –20.9°[12,14]. This delocalization is also responsible for the lengthening of the bond distance Nsp^2-Csp^2, N–C1: 1.274 (2) Å, and the shortening of the bond distance Nsp^2-Csp^3, N–C4: 1.452 (2) Å. Analogous deviations were observed in similar oxazine compounds[12,14,15].

The three phenyl rings are planar and show normal bond lengths. The two hydrogen atoms of the oxazine ring are in equatorial (H2) and axial position (H3), in a *„cis"* configuration (cf. Fig. 2), as was inferred from the NMR data.

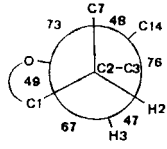


Fig. 2. Newman projection of C2–C3 bond with torsion angles (°)

In conclusion, the present work illustrates the potential of 2-aza-1,3-butadienes in organic synthesis. The reaction of **2** with aldehydes allows the preparation of 5,6-dihydro-2*H*-1,3-oxazine derivatives **4** and **5** which are scarcely found in the literature[16].

Experimental Part

IR spectra: Pye Unicam SP 1025. – ^{1}H- and ^{13}C-NMR spectra: Varian FT-80A and Varian V77 XL 300 spectrometers, δ scale, internal reference tetramethylsilane. – MS: Finnigan MAT CH5 and Hewlett-Packard 5930A. – Melting points: Uncorrected. – Elemental analyses: Perkin-Elmer 240.

General Preparative Procedure of 2-Aza-1,3-butadienes **2**: A solution of 20 mmol of imine **1** in 20 ml of dry THF is heated, in an argon atmosphere, under reflux for two hours with catalytic amounts of trifluoroacetic acid (0.15 ml, 2 mmol). Evaporation of solvents under reduced pressure and high vacuum distillation affords pure 2-aza-1,3-butadienes **2**.

3,5-Diphenyl-4-aza-2,4-heptadiene (**2a**): From ethyl phenyl ketimine (2.66 g, 20 mmol) as described in the general procedure. Yield 2.39 g (96%) of green oil; b.p. 127–130°C/10^{-3} Torr. – IR (film): 1640 cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 0.9 (t, 3H); 1.6 (d, 3H); 2.6 (q, 2H); 5.4 (q, 1H); 7.1–8.0 (m, 10H). – ^{13}C NMR (Pure + cap. D_2O): δ = 169.9 (s); 147.5 (s); 138.4 (s); 137.6 (s); 130.0–124.8 (m); 102.5 (d); 23.3 (t); 12.8 (q); 11.3 (q). – MS (EI) = 249 (M^+).

$C_{18}H_{19}N$ (249.4) Calc. C 86.70 H 7.68 N 5.62 Found C 86.57 H 7.70 N 5.55

3,5-Bis(4-methylphenyl)-4-aza-2,4-heptadiene (**2b**): From ethyl (4-methylphenyl) ketimine (2.94 g, 20 mmol). Yield 2.68 g (97%) of green oil; b.p. 138–141°C/10^{-3} Torr. – IR (film): 1635 cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 0.9 (t, 3H); 1.6 (d, 3H); 2.3 (s, 3H); 2.4 (s, 3H); 2.6 (q, 2H); 5.4 (q, 1H); 6.9–8.0 (m, 8H). – ^{13}C NMR (Pure + cap. D_2O): δ = 169.1 (s); 147.6 (s); 139.6 (s); 136.1 (s); 135.8 (s); 135.0 (s); 128.7–124.7 (m); 101.1 (d); 23.1 (t); 21.0 (q); 20.1 (q); 12.7 (q); 11.5 (q).

$C_{20}H_{23}N$ (277.4) Calc. C 86.59 H 8.36 N 5.05 Found C 86.65 H 8.31 N 5.20

4,6-Diphenyl-5-aza-3,5-nonadiene (**2c**): From phenyl propyl ketimine (2.94 g, 20 mmol). Yield 2.69 g (97%) of green oil; b.p. 144–147°C/10^{-3} Torr. – IR (film): 1640 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 0.7 (t, 3H); 1.1 (t, 3H); 1.3 (m, 2H); 2.0 (t, 2H); 2.6 (q, 2H); 5.3 (t, 1H); 7.0–8.0 (m, 10H). – ^{13}C NMR ($CDCl_3$): δ = 169.1 (s); 145.5 (s); 138.3 (s); 137.9 (s); 129.4–124.5 (m); 110.5 (d); 32.0 (t); 20.2 (t); 19.8 (t); 13.5 (q); 13.3 (q).

$C_{20}H_{23}N$ (277.4) Calc. C 86.59 H 8.36 N 5.05 Found C 86.48 H 8.40 N 5.15

2,4-Dicyclohexyl-1,5-diphenyl-3-aza-1,3-pentadiene (**2d**): From benzyl cyclohexyl ketimine (4.03 g, 20 mmol). Yield 3.66 g (95%) of yellow oil; b.p. 172–175°C/10^{-3} Torr. – IR (film): 1670 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 0.7–2.2 (m, 22H); 3.2 (s, 2H); 5.2 (s, 1H); 6.4–7.3 (m, 10H). – ^{13}C NMR ($CDCl_3$): δ = 171.9 (s); 154.1 (s); 137.9 (s); 134.7 (s); 129.0–124.5 (m); 104.7 (d); 46.6 (d); 44.2 (d); 39.4 (t); 31.8–26.1 (m). – MS (EI) = 385 (M^+).

$C_{28}H_{35}N$ (385.6) Calc. C 87.22 H 9.15 N 3.63 Found C 87.30 H 9.03 N 3.71

4,6-Dipropyl-5-aza-3,5-nonadiene (**2e**): From dipropyl ketimine (2.26 g, 20 mmol). Yield 2.01 g (96%) of colourless liquid; b.p. 50–51°C/10^{-2} Torr. – IR (film): 1660 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 0.7–2.3 (m, 26H); 4.2 (t, 1H). – ^{13}C NMR ($CDCl_3$): δ = 170.5 (s); 147.9 (s); 108.5 (d); 42.6–36.3 (m); 21.9–20.5 (m); 15.2–14.9 (m). – MS (CI) = 210 ($M^+ + 1$).

$C_{14}H_{27}N$ (209.4) Calc. C 80.31 H 13.00 N 6.69 Found C 80.42 H 12.93 N 6.72

3,5-Dicyclohexyl-4-aza-2,4-heptadiene (**2f**) *and 3-Cyclohexyl-5-cyclohexylidene-4-aza-3-hepten* (**2f'**): From cyclohexyl ethyl ketimine (2.78 g, 20 mmol). Yield 2.43 g (93%) of colourless oil; b.p. 111–114°C/10^{-3} Torr. – IR (film): 1660 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 0.6–2.4 (m, 30H); 4.3 (q, 1H). – ^{13}C NMR ($CDCl_3$): δ = 175.4 (s); 175.1 (s); 154.7 (s); 141.7 (s); 113.8 (s); 97.5 (d); 46.3–43.2 (m); 33.1–25.5 (m); 14.1–9.7 (m). – MS (EI) = 261 (M^+).

$C_{18}H_{31}N$ (261.4) Calc. C 82.69 H 11.95 N 5.36 Found C 82.57 H 12.02 N 5.41

General Preparative Procedure of 5,6-Dihydro-2H-1,3-oxazine Derivatives **4** *and* **5**: All runs were carried out under argon. To a solution of 2-aza-1,3-butadiene **2** (10 mmol) in dry benzene (10 ml), aldehyde **3** (11 mmol) dissolved in dry benzene (10 ml) and boron trifluoride etherate (1 mmol) was added at room temperature. When both additions were finished, the mixture was refluxed for 1–2 days, hydrolysed with ice cooled 3 N KOH and extracted with ether.

The organic layer was dried over sodium sulfate, filtered and evaporated under reduced pressure to afford an oily residue which by washing with hexane yields the 5,6-dihydro-2*H*-1,3-oxazines as colourless solids. Recrystallization from a hot mixture of hexane/chloroform (6/1) produces the pure oxazine derivatives as colourless solids.

In some cases, the reaction was also carried out without boron trifluoride etherate following the same procedure, thus observing a lowering in the yield (Compounds **4a–d**).

(2R,5R,6S/2S,5S,6R)-2-Ethyl-5,6-dihydro-5-methyl-2,4,6-triphenyl-2H-1,3-oxazine (**4a**): From **2a** (2.5 g, 10 mmol), benzaldehyde (1.1 ml, 11 mmol) and boron trifluoride etherate (0.12 ml, 1 mmol) as described in the general procedure. Yield 3.37 g (95%). Yield in the absence of boron trifluoride etherate 2.84 g (80%). – M.p. 172–174°C. – IR (Nujol): 1640; 1010 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 0.9 (d, 3H); 1.0 (t, 3H); 2.1 (q, 2H); 3.0 (qd, 1H, J_1 = 6.3 Hz, J_2 = 3.1 Hz); 4.7 (d, 1H; J = 3.1 Hz); 7.1–8.1 (m, 15H). – ^{13}C NMR ($CDCl_3$): δ = 165.5 (s); 145.1 (s); 140.2 (s); 137.6 (s); 130.0–125.5 (m); 93.7 (s); 70.9 (d); 38.1 (t); 34.5 (d); 12.5 (q); 8.4 (q). – MS (EI) = 326 (M^+ – 29).

$C_{25}H_{25}NO$ (355.5) Calc. C 84.47 H 7.09 N 3.94 Found C 84.56 H 6.98 N 3.99

(2R,5R,6S/2S,5S,6R)-6-(4-Chlorophenyl)-2-ethyl-5,6-dihydro-5-methyl-2,4-diphenyl-2H-1,3-oxazine (**4b**): From **2a** (2.5 g, 10 mmol), 4-chlorobenzaldehyde (1.3 ml, 11 mmol) and boron trifluoride etherate (0.12 ml, 1 mmol). Yield 3.31 g (85%). Yield in the absence of boron trifluoride etherate 3.04 g (78%). – M.p. 151–153°C. – IR (Nujol): 1640; 1010 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 0.9 (d, 3H); 1.0 (t, 3H); 2.1 (q, 2H); 3.0 (qd, 1H, J_1 = 6.3 Hz, J_2 = 3.1 Hz); 4.6 (d, 1H, J = 3.1 Hz); 7.1–8.1 (m, 14H). – ^{13}C NMR ($CDCl_3$): δ = 165.2 (s); 144.9 (s); 138.6 (s); 137.7 (s); 132.7 (s); 130.1–126.5 (m); 93.8 (s); 70.5 (d); 38.0 (t); 34.3 (d); 12.4 (q); 8.4 (q). – MS (EI) = 360 (M^+ – 29). – MS (CI) = 390 (M^+ + 1).

$C_{25}H_{24}ClNO$ (389.9) Calc. C 77.01 H 6.20 Cl 9.09 N 3.59
Found C 77.05 H 6.68 Cl 8.83 N 3.39

(2R,5R,6S/2S,5S,6R)-2-Ethyl-5,6-dihydro-5-methyl-6-(4-nitrophenyl)-2,4-diphenyl-2H-1,3-oxazine (**4c**): From **2a** (2.5 g, 10 mmol), 4-nitrobenzaldehyde (1.7 g, 11 mmol) and boron trifluoride etherate (0.12 ml, 1 mmol). Yield 3.60 g (90%). Yield in the absence of boron trifluoride etherate 3.32 g (83%). – M.p. 146–148°C. – IR (Nujol): 1640; 1515, 1010 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 0.9 (d, 3H); 1.0 (t, 3H); 2.2 (q, 2H); 3.1 (qd, 1H, J_1 = 6.3 Hz, J_2 = 3.1 Hz); 4.8 (d, 1H, J = 3.1 Hz); 7.1–8.4 (m, 14H). – ^{13}C NMR ($CDCl_3$): δ = 164.8 (s); 147.5 (s); 147.2 (s); 144.5 (s); 137.2 (s); 130.2–123.4 (m); 94.1 (s); 70.7 (d); 37.9 (t); 34.2 (d); 12.5 (q); 8.3 (q). – MS (EI) = 371 (M^+ – 29).

$C_{25}H_{24}N_2O_3$ (400.5) Calc. C 74.98 H 6.04 N 6.99 Found C 74.86 H 6.01 N 7.11

(2R,5R,6S/2S,5S,6R)-2-Ethyl-5,6-dihydro-5-methyl-2,4-diphenyl-6-(4-pyridinyl)-2H-1,3-oxazine (**4d**): From **2a** (2.5 g, 10 mmol), 4-pyridinecarbaldehyde (1.0 ml, 11 mmol) and boron trifluoride etherate (0.12 ml, 1 mmol). Yield 3.17 g (89%). Yield in the absence of boron trifluoride etherate 2.74 g (77%). – M.p. 174–176°C. – IR (Nujol): 1640; 1010 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 0.9 (d, 3H); 1.0 (t, 3H); 2.1 (q, 2H); 3.0 (qd, 1H, J_1 = 6.3 Hz, J_2 = 3.1 Hz); 4.7 (d, 1H, J = 3.1 Hz); 7.1–8.7 (m, 14H). – ^{13}C NMR ($CDCl_3$): δ = 164.9 (s); 149.8 (s); 149.1 (d); 144.6 (s); 137.3 (s); 130.2–126.6 (m); 120.7 (d); 94.0 (s); 70.2 (d); 37.9 (t); 33.9 (d); 12.5 (q); 8.3 (q). – MS (EI) = 327 (M^+ – 29).

$C_{25}H_{24}N_2O$ (356.5) Calc. C 80.87 H 6.79 N 7.86 Found C 80.98 H 6.56 N 7.96

(2R,5R,6S/2S,5S,6R)-2-Ethyl-5,6-dihydro-5-methyl-6-(4-methylphenyl)-2,4-diphenyl-2H-1,3-oxazine (**4e**): From **2a** (2.5 g, 10 mmol), 4-methylbenzaldehyde (1.30 ml, 11 mmol) and boron trifluoride etherate (0.12 ml, 1 mmol). Yield 2.77 g (75%). – M.p. 90–92°C. – IR (Nujol): 1635; 1010 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 0.9 (d, 3H); 1.0 (t, 3H); 2.1 (q, 2H); 2.3 (s, 3H); 3.0 (qd, 1H, J_1 = 6.3 Hz, J_2 = 3.1 Hz); 4.7 (d, 1H, J = 3.1 Hz); 6.9–8.0 (m, 14H). – ^{13}C NMR ($CDCl_3$): δ = 165.6 (s); 145.2 (s); 137.6 (s); 137.1 (s); 136.3 (s); 129.9–125.4 (m); 93.7 (s); 70.9 (d); 38.1 (t); 34.5 (d); 21.1 (q); 12.6 (q); 8.4 (q).

$C_{26}H_{27}NO$ (369.5) Calc. C 84.51 H 7.37 N 3.79 Found C 84.42 H 7.30 N 3.89

(2R,5R,6S/2S,5S,6R)-2-Ethyl-6-(2-furyl)-5,6-dihydro-5-methyl-2,4-diphenyl-2H-1,3-oxazine (**4f**): From **2a** (2.5 g, 10 mmol), 2-furaldehyde (0.91 ml, 11 mmol) and boron trifluoride etherate (0.12 ml, 1 mmol). Yield 2.62 g (76%). – M.p. 103–105°C. – IR (Nujol): 1640; 1010 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 0.9 (d, 3H); 1.0 (t, 3H); 2.1 (q, 2H); 3.0 (qd, 1H, J_1 = 6.3 Hz, J_2 = 3.1 Hz); 4.7 (d, 1H, J = 3.1 Hz); 6.5–8.0 (m, 13H). – ^{13}C NMR ($CDCl_3$): δ = 164.9 (s); 153.3 (s); 144.7 (s); 141.4 (d); 130.0 (s); 128.3–126.5 (m); 110.1 (d); 106.4 (d); 94.5 (s); 67.7 (d); 37.8 (t); 32.8 (d); 13.1 (q); 8.3 (q). – MS (EI) = 345 (M^+).

$C_{23}H_{23}NO_2$ (345.5) Calc. C 79.97 H 6.71 N 4.05 Found C 80.10 H 6.80 N 3.92

(2R,5R,6S/2S,5S,6R)-2-Ethyl-5,6-dihydro-5-methyl-2,4-diphenyl-6-(2-thienyl)-2H-1,3-oxazine (**4g**): From **2a** (2.5 g, 10 mmol), 2-thiophenecarbaldehyde (1.0 ml, 11 mmol) and boron trifluoride etherate (0.12 ml, 1 mmol). Yield 2.92 g (81%). – M.p. 127–129°C. – IR (Nujol): 1640; 1010 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 0.9 (t, 3H); 1.0 (d, 3H); 2.1 (q, 2H); 3.0 (qd, 1H, J_1 = 6.3 Hz, J_2 = 3.1 Hz); 4.8 (d, 1H, J = 3.1 Hz); 6.8–8.0 (m, 13H). – ^{13}C NMR ($CDCl_3$): δ = 164.9 (s); 144.8 (s); 143.6 (s); 137.2 (s); 130.0 (d); 128.3–126.6 (m); 123.7 (d); 122.4 (d); 94.0 (s); 69.3 (d); 37.9 (t); 34.9 (d); 12.6 (q); 8.3 (q).

$C_{23}H_{23}NOS$ (361.5) Calc. C 76.42 H 6.41 N 3.87 Found C 76.58 H 6.30 N 3.99

(2R,5R,6R/2S,5S,6S)-6-n-Butyl-2-ethyl-5,6-dihydro-5-methyl-2,4-diphenyl-2H-1,3-oxazine (**4h**): From **2a** (2.5 g, 10 mmol), valeraldehyde (1.2 ml, 11 mmol) and boron trifluoride etherate (0.12 ml, 1 mmol). Yield 2.34 g (70%) of a yellow oil. B.p. 152–155°C/10^{-3} Torr. – IR (film): 1640; 1010 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 0.7–2.2 (m, 14H); 2.5 (qd, 1H, J_1 = 7.8 Hz, J_2 = 3.1 Hz); 3.3 (td, 1H, J_1 = 6.3 Hz, J_2 = 3.1 Hz); 6.9–8.0 (m, 10H). – ^{13}C NMR ($CDCl_3$): δ = 165.5 (s); 145.8 (s); 137.4 (s); 128.1–125.6 (m); 92.9 (s); 69.1 (d); 37.7 (t); 31.7 (d); 31.5 (t); 27.6 (t); 22.6 (t); 13.9 (q); 11.7 (q); 8.4 (q). – MS (EI) = 306 (M^+ – 29).

$C_{23}H_{29}NO$ (335.5) Calc. C 82.34 H 8.71 N 4.17 Found C 82.50 H 8.62 N 4.29

(2R,5R,6R/2S,5S,6S)-2-Ethyl-5,6-dihydro-6-isopropyl-5-methyl-2,4-diphenyl-2H-1,3-oxazine (**4i**): From **2a** (2.5 g, 10 mmol), isobutyraldehyde (1.0 ml, 11 mmol) and boron trifluoride etherate (0.12 ml, 1 mmol). Yield 2.41 g (75%). – M.p. 105–107°C. – IR (Nujol): 1640; 1010 cm^{-1}. – ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.8 (d, 3H); 0.9 (t, 3H); 1.1 (d, 3H); 1.2 (d, 3H); 1.9 (m, 1H); 2.0 (m, 2H); 2.8 (qd, 1H, J_1 = 7.1 Hz, J_2 = 2.6 Hz); 2.9 (dd, 1H, J_1 = 9.9 Hz, J_2 = 2.6 Hz); 7.2–8.0 (m, 10H). – ^{13}C NMR ($CDCl_3$): δ = 165.9 (s); 145.7 (s); 138.0 (s); 129.8–126.7 (m); 93.3 (s); 75.2 (d); 37.9 (t); 31.0 (d); 29.1 (d); 19.9 (q); 17.8 (q); 11.7 (q); 8.4 (q). – MS (EI) = 292 (M^+ – 29). – MS (CI) = 322 (M^+ + 1).

$C_{22}H_{27}NO$ (321.5) Calc. C 82.20 H 8.47 N 4.36 Found C 82.33 H 8.40 N 4.25

(2R,5R,6S/2S,5S,6R)-6-(1-Chloropropyl)-2-ethyl-5,6-dihydro-5-methyl-2,4-diphenyl-2H-1,3-oxazine (**4j**): From **2a** (2.5 g, 10 mmol), 2-chlorobutyraldehyde (2.01 ml of a 5.3 M solution in THF prepared as described in the literature[17], 11 mmol) and boron trifluoride etherate (0.12 ml, 1 mmol). Yield 2.77 g (78%). – M.p. 126–128°C. – IR (Nujol): 1640; 1010 cm^{-1}. – ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.88 (t, 3H); 0.98 (t, 3H); 1.21 (d, 3H); 1.56 (m, 1H); 2.03 (m, 2H); 2.34 (m, 1H); 3.19 (qd, 1H, J_1 7.1 Hz, J_2 = 2.6 Hz); 3.43 (dd, 1H, J_1 = 10.1 Hz, J_2 = 2.6 Hz); 3.87 (td, 1H, J_1 = 9.6 Hz, J_2 = 2.6 Hz); 7.2–8.0 (m, 10H). – ^{13}C NMR ($CDCl_3$): δ = 165.9 (s); 144.7 (s); 137.4 (s); 128.4–126.8 (m); 94.3 (s); 72.1 (d); 62.5 (d); 37.4 (t); 30.9 (d); 27.0 (t); 11.4 (q); 10.2 (q); 8.4 (q). – MS (CI) = 356 (M^+ + 1).

$C_{22}H_{26}ClNO$ (355.9) Calc. C 74.24 H 7.36 Cl 9.96 N 3.94
Found C 74.10 H 7.29 Cl 9.82 N 3.99

(2R,5R,6R/2S,5S,6S)-2-Ethyl-5,6-dihydro-5-methyl-2,4-diphenyl-6-(1-phenylethyl)-2H-1,3-oxazine (**4k**): From **2a** (2.5 g, 10 mmol), 2-phenylpropanal (1.5 ml, 11 mmol) and boron trifluoride etherate (0.12 ml, 1 mmol). Yield 2.99 g (78%). – M.p. 152–154°C. – IR (Nujol): 1640; 1010 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 0.9 (t, 3H); 1.1 (d, 3H); 1.3 (d, 3H); 2.0 (q, 2H); 2.4 (qd, 1H, J_1 = 6.3 Hz, J_2 = 3.1 Hz); 2.9 (m, 1H); 3.5 (dd, 1H, J_1 = 9.9 Hz, J_2 = 3.1 Hz); 6.9–7.7 (m, 15H). – ^{13}C NMR ($CDCl_3$): δ = 165.9 (s); 145.5 (s); 143.6 (s); 137.3 (s); 129.8–126.4 (m); 93.5 (s); 73.8 (d); 41.7 (d); 37.9 (t); 30.7 (d); 20.8 (q); 11.9 (q); 8.5 (q).

$C_{27}H_{29}NO$ (383.5) Calc. C 84.56 H 7.62 N 3.65 Found C 84.38 H 7.69 N 3.72

(2R,5R,6S/2S,5S,6R)-5-Ethyl-5,6-dihydro-2,4,6-triphenyl-2-n-propyl-2H-1,3-oxazine (**4l**): From **2c** (2.8 g, 10 mmol), benzaldehyde (1.1 ml, 11 mmol) and boron trifluoride etherate (0.12 ml, 1 mmol). Yield 3.26 g (85%). – M.p. 96–98°C. – IR (Nujol): 1650; 1010 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 0.4 (t, 3H); 0.8 (t, 3H); 1.2–1.8 (m, 4H); 2.0 (qd, 2H, J_1 = 7.1 Hz, J_2 = 3.1 Hz); 2.8 (td, 1H, J_1 = 7.8 Hz, J_2 = 3.1 Hz); 4.6 (d, 1H, J = 3.1 Hz); 7.1–8.0 (m, 15H). – ^{13}C NMR ($CDCl_3$): δ = 164.8 (s); 145.1 (s); 140.2 (s); 138.4 (s); 129.9–125.6 (m); 93.5 (s); 71.3 (d); 47.5 (t); 41.1 (d); 20.8 (t); 17.2 (t); 14.4 (q); 13.2 (q). – MS (CI) = 384 (M^+ + 1).

$C_{27}H_{29}NO$ (383.5) Calc. C 84.55 H 7.62 N 3.65 Found C 84.40 H 7.69 N 3.70

(2R,5R,6S/2S,5S,6R)-2-Ethyl-5,6-dihydro-5-methyl-2,4-bis(4-methylphenyl)-6-phenyl-2H-1,3-oxazine (**4m**): From **2b** (2.8 g, 10 mmol), benzaldehyde (1.1 ml, 11 mmol) and boron trifluoride etherate (0.12 ml, 1 mmol). Yield 3.07 g (80%). – M.p. 106–108°C. – IR (Nujol): 1640; 1010 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 0.9 (d, 3H); 1.0 (t, 3H); 2.1 (q, 2H); 2.3 (s, 3H); 2.4 (s, 3H); 3.0 (qd, 1H, J_1 = 6.3 Hz, J_2 = 3.1 Hz); 4.7 (d, 1H, J = 3.1 Hz); 7.0–8.0 (m, 13H). – ^{13}C NMR ($CDCl_3$): δ = 165.2 (s); 142.3 (s); 140.2 (s); 139.9 (s); 136.4 (s); 134.9 (s); 129.0–125.4 (m); 93.6 (s); 70.8 (d); 38.1 (t); 34.4 (d); 21.1 (q); 20.9 (q); 12.6 (q); 8.4 (q). – MS (EI) = 354 (M^+ – 29). – MS (CI) = 384 (M^+ + 1).

$C_{27}H_{29}NO$ (383.5) Calc. C 84.56 H 7.62 N 3.65 Found C 84.45 H 7.72 N 3.72

(2R,5R,6S/2S,5S,6R)-2-Ethyl-5,6-dihydro-5-methyl-2,4,6-tris(4-methylphenyl)-2H-1,3-oxazine (**4n**): From **2b** (2.8 g, 10 mmol), 4-methylbenzaldehyde (1.30 ml, 11 mmol) and boron trifluoride etherate (0.12 ml, 1 mmol). Yield 2.98 g (75%). – M.p. 125–127°C. – IR (Nujol): 1640; 1010 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 0.9 (d, 3H); 1.0 (t, 3H); 2,1 (q, 2H); 2.2 (s, 3H); 2.3 (s, 6H); 2.9 (qd, 1H, J_1 = 6.3 Hz, J_2 = 3.1 Hz); 4.6 (d, 1H, J = 3.1 Hz); 6.9–7.9 (m, 12H). – ^{13}C NMR ($CDCl_3$): δ = 165.1 (s); 142.4 (s); 139.8 (s); 137.2 (s); 136.3 (s); 136.1 (s); 134.9 (s); 129.0–124.9 (m); 93.6 (s); 70.8 (d); 38.2 (t); 34.1 (d); 21.1 (q); 20.9 (q); 12.6 (q); 8.4 (q). – MS (CI) = 398 (M^+ + 1).

$C_{28}H_{31}NO$ (397.6) Calc. C 84.59 H 7.86 N 3.52 Found C 84.45 H 7.94 N 3.62

(2R,5R,6S/2S,5S,6R)-2-Ethyl-5,6-dihydro-6-(4-methoxyphenyl)-5-methyl-2,4-bis(4-methylphenyl)-2H-1,3-oxazine (**4o**): From **2b** (2.8 g, 10 mmol), 4-methoxybenzaldehyde (1.34 ml, 11 mmol) and boron trifluoride etherate (0.12 ml, 1 mmol). Yield 2.98 g (72%). – M.p. 103–105°C. – IR (Nujol): 1640; 1010 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 0.9 (d, 3H); 1.0 (t, 3H); 2.1 (q, 2H); 2.2 (s, 3H); 2.3 (s, 3H); 2.9 (qd, 1H, J_1 = 6.3 Hz, J_2 = 3.1 Hz); 3.7 (s, 3H); 4.6 (d, 1H, J = 3.1 Hz); 7.0–8.0 (m, 12H). – ^{13}C NMR ($CDCl_3$): δ = 165.3 (s); 158.6 (s); 142.4 (s); 139.9 (s); 136.4 (s); 135.0 (s); 132.3 (s); 129.0–126.6 (m); 113.6 (d); 93.6 (s); 70.6 (d); 54.9 (q); 38.1 (t); 34.5 (d); 21.1 (q); 21.0 (q); 12.6 (q); 8.4 (q).

$C_{28}H_{31}NO_2$ (413.6) Calc. C 81.32 H 7.55 N 3.39 Found C 81.40 H 7.48 N 3.32

(2R,5S,6S/2S,5R,6R)-2-Benzyl-2,4-dicyclohexyl-5,6-dihydro-5,6-diphenyl-2H-1,3-oxazine (**5a**) *and (2R,5R,6R/2S,5S,6S)-2-Benzyl-2,4-dicyclohexyl-5,6-dihydro-5,6-diphenyl-2H-1,3-oxazine* (**5b**): From **2d** (3.85 g, 10 mmol), benzaldehyde (1.1 ml, 11 mmol) and boron trifluoride etherate (0.12 ml, 1 mmol). Yield 4.22 g (86%) of a 2.5/1 **5a**/**5b** mixture. – IR (Nujol): 1660; 1060 cm^{-1}. – ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.82–2.26 (m, 44H); 2.70 (d, 1H, J = 9.7 Hz)[18]; 3.05 (d, 1H (CH_2), J = 12.6 Hz); 3.10 (d, 1H, J = 9.7 Hz)[18]; 3.15 (d, 1H, (CH_2), J = 13.3 Hz); 3.16 (d, 1H (CH_2), J = 12.6 Hz); 3.35 (d, 1H (CH_2), J = 13.3 Hz); 4.10 (d, 1H, J = 9.7 Hz)[18]; 4.56 (d, 1H, J = 9.7 Hz)[18]; 6.41–7.33 (m, 30H). – ^{13}C

NMR ($CDCl_3$): δ = 170.6 (s); 168.9 (s); 141.9 (s); 138.3 (s); 138.0 (s); 137.8 (s); 131.8–125.7 (m); 92.5 (s); 92.3 (s); 75.7 (d); 75.5 (d); 51.1 (d); 50.6 (d); 48.0 (d); 47.2 (d); 43.7 (t); 43.6 (t); 32.3–25.4 (m). – MS (CI) = 492 ($M^+ + 1$).

$C_{35}H_{41}NO$ (491.7) Calc. C 85.49 H 8.40 N 2.85 Found C 85.36 H 8.46 N 2.92

X-Ray Diffraction Analysis of **4a**[*]: Colourless crystals of **4a** were obtained from recrystallization in toluene. Crystal data: $C_{25}H_{25}NO$; m.w. = 355.484; triclinic; $P\bar{1}$; a = 10.1459 (9) Å; b = 11.2989 (6) Å; c = 10.091 (1) Å; α = 99.744 (7)°; β = 116.419 (7)°; γ = 71.767 (5)°; V = 983.33 Å^3; Z = 2; $d_{calc.}$ = 1.20 g cm^{-3}; μ(Cu-K_α) = 5.24 cm^{-1}; λ = 1.54178 Å. Measured reflexions (4.1 ≤ Θ ≤ 75.6) = 4084; observed reflexions ($I \geq 2\sigma(I)$) = 3378.

Structure solution obtained by SHELX 84 program (*Sheldrick*, to be published (1984)); anisotropic refinement for all non-hydrogen atoms (244 parameters), converged to R = 0.053 and R_w = 0.078 (res. el. dens.: 0.21 e Å^{-3}).

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[*] Further details and basic data concerning the X-ray analysis may be obtained from Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen (W. Germany), by specifying registry number CSD 51109, author, and source.

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[7] Heating for more than 15 days of **2a** with either 4-methylbenzaldehyde or 2-methylpropanol in benzene and in the absence of catalyst did not lead to the formation of appreciable amounts of corresponding cycloadduct **4**.

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