Synthesis of 2-Substituted 4*H*-3,1-Benzoxazin-4-ones by Thermally Induced Cyclization of *N*-(2-Benzyloxycarbonyl)phenyl Ketenimines; Oxygen-to-Carbon Migration of a Benzyl Group

Mateo Alajarín,*[a] Ángel Vidal,*[a] María-Mar Ortín,[a] Delia Bautista[b]

[a] Departamento de Química Orgánica, Facultad de Química, Universidad de Murcia, Campus de Espinardo, 30100 Murcia, Spain

[b] Servicio Universitario de Instrumentación Científica, Universidad de Murcia, Campus de Espinardo, 30100 Murcia, Spain
Fax +34(968)364149; E-mail: alajarin@um.es

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Abstract: *N*-(2-Benzyloxycarbonyl)phenyl ketenimines undergo a thermally induced cyclization to give 2-substituted 4*H*-3,1-benzoxazin-4-ones. These processes involve the formation of a new carbon–oxygen bond and the migration of the benzyl group from the oxygen atom of the benzyloxy unit at the ester function to the terminal carbon atom of the ketenimine fragment.

Key words: azides, ketenimines, cyclizations, rearrangements, benzoxazinones

4*H*-3,1-Benzoxazin-4-ones (also known by the common name 'acylanthranils'), particularly those with a carbon substituent at the 2-position, are important fused heterocycles. Compounds possessing this heterocyclic ring system are found in nature, as the phytoalexins avenalumin I[1] and dianthalexin,[2] and some hydroxylated derivatives of this last compound.[3] The 3,1-benzoxazin-4-one core is a key structural fragment in a range of biologically active compounds. Some derivatives of this family act as competitive inhibitors[4] or potent inactivators[5] of chymotrypsin and other serine proteases, or are inhibitors of human leukocyte elastase (HLE),[6] herpes simplex virus type 1 (HSV-1) protease,[7] and C1r serine protease.[8] Moreover, some 2-substituted 4*H*-3,1-benzoxazin-4-ones have the ability to lower the levels of cholesterol and triglycerides in plasma, and to raise the proportion of total cholesterol carried by high-density lipoproteins.[9] The importance of these benzoxazinones also reside in that these compounds are useful precursors for the preparation of other pharmaceutically active heterocyclic compounds, mainly quinazoline and quinoline derivatives.[10]

Different general protocols have been reported for the preparation of 4*H*-3,1-benzoxazin-4-ones bearing a carbon substituent at C2,[11] such as the condensation of anthranilic acids with acid anhydrides, orthoesters or acid chlorides,[12] the cyclodehydration of *N*-acylanthranilic acids,[13] or those that use the closely related 2*H*-3,1-benzoxazine-2,4(1*H*)dione system (isatoic anhydride) as starting material.[14] Other synthetic methods involve the thallation and subsequent Pd-catalyzed carbonylation of acetanilide,[15] the Pd-catalyzed cyclocarbonylation of *ortho*-iodoanilines with unsaturated halides or triflates[16] or with acid chlorides,[17] the oxidation from 3-oxoindolines and indoles,[18] [4+2] cycloaddition reactions of the imino-ketene resulting from the thermolysis of benzotriazinone,[19] the condensation of 2-azidobenzoic acid with aldehydes,[20] or the electrochemical cyclization of *N*-acyl-2-trichloroacetylanilines.[21]

Ketenimines have been frequently used as precursors of nitrogen-containing heterocycles.[22] As a matter of fact we have successfully employed these heterocumulenes in the synthesis of a variety of nitrogenated heterocycles. For instance, we have prepared isoquinolines by electrocyclic ring closure of ketenimines,[23] azeto[2,1-*b*]quinazolines via intramolecular imino-ketenimine [2+2] cycloaddition,[24] benz[*b*]acridines,[25] benzimidazo[1,2-*b*]isoquinolines,[26] or pyrido[1,2-*a*]benzimidazoles[27] through [4+2] cycloaddition reactions, and indoles or 1,4-benzoxazines by intramolecular addition of carbon centered radicals onto ketenimines.[28]

Here we report a new synthesis of 2-substituted 4*H*-3,1-benzoxazin-4-ones based on the thermally induced cyclization of *N*-(2-benzyloxycarbonyl)phenyl ketenimines. These processes involve the thermal rearrangement of an *O*-benzyl group to a carbon atom.

The reaction of 2-azidobenzoyl chloride (**1a**) and 2-azido-5-chlorobenzoyl chloride (**1b**) with benzylic alcohols **2**, in CH_2Cl_2 solution, in the presence of a slight excess of 4-dimethylaminopyridine, provided benzyl 2-azidobenzoates **3** in good to excellent yields (Table 1). CH_2Cl_2 solutions of **3** were treated, at room temperature, with triphenylphosphane to give triphenylphosphazenes **4**. The transformation **3** → **4** was complete in about 16 hours, as followed by IR (disappearance of the azide vibration near 2100 cm^{-1}, and observation of the new bands at 1438 cm^{-1} and 1121 cm^{-1} corresponding to the phosphazene groups). Treatment of the resulting solutions containing compounds **4** with a stoichiometric amount of diphenylketene or methylphenylketene afforded *N*-(2-benzyloxycarbonyl)phenyl ketenimines **5**. The formation of ketenimines **5** was established by IR spectroscopy: the IR spectra of the reaction mixtures showed very strong absorptions around 2000 cm^{-1} attributable to the N=C=C group. After removal of the solvent, the mixtures containing the *N*-(2-benzyloxycarbonyl)phenyl ketenimines **5** and triphenylphosphane oxide were heated at 200 °C, in a

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Table 1 Benzyl 2-Azidobenzoates **3**

Compound	R^1	Ar	Yield (%)
3a	H	4-MeC_6H_4	82
3b	H	4-$MeOC_6H_4$	75
3c	H	3,4-$(MeO)_2C_6H_3$	91
3d	Cl	4-MeC_6H_4	70
3e	Cl	4-$MeOC_6H_4$	80
3f	Cl	3,4-$(MeO)_2C_6H_3$	60
3g	Cl	3,5-$(MeO)_2C_6H_3$	78

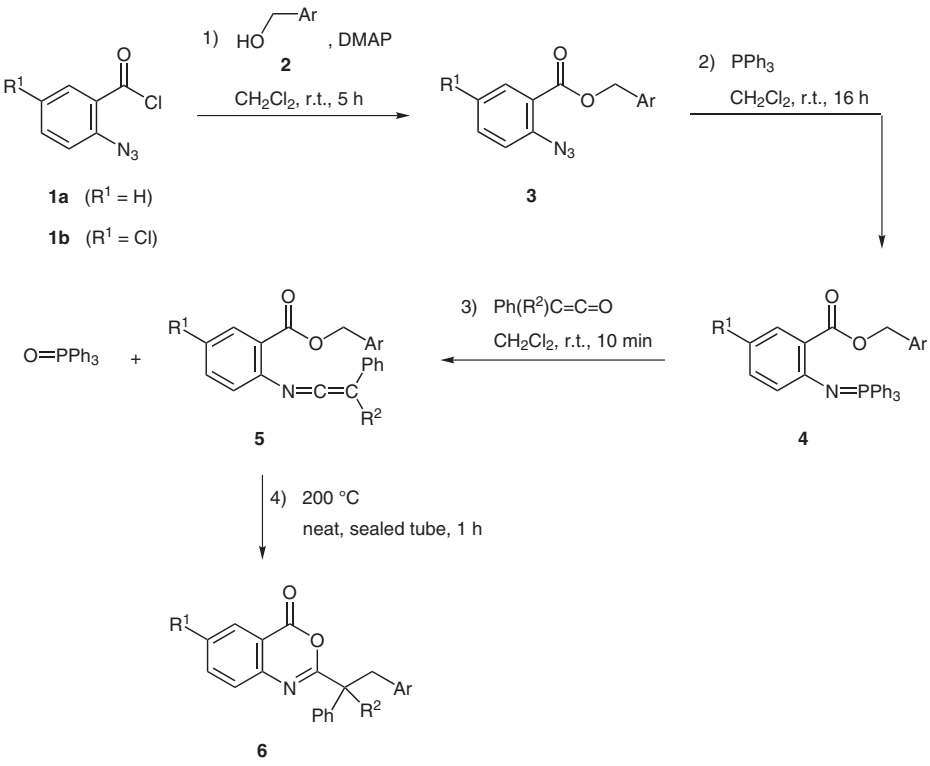
Table 2 2-Substituted 4*H*-3,1-Benzoxazin-4-ones **6**

Compound	R^1	R^2	Ar	Yield (%)[a,b]
6a	H	Ph	4-MeC_6H_4	45
6b	H	Me	4-MeC_6H_4	43
6c	H	Ph	4-$MeOC_6H_4$	41
6d	H	Ph	3,4-$(MeO)_2C_6H_3$	42
6e	Cl	Ph	4-MeC_6H_4	50
6f	Cl	Ph	4-$MeOC_6H_4$	40
6g	Cl	Ph	3,4-$(MeO)_2C_6H_3$	43
6h	Cl	Ph	3,5-$(MeO)_2C_6H_3$	40

[a] Global yield for the conversion **3** → **6**.
[b] Isolated yield after silica gel column chromatography.

sealed tube, for one hour.[29] The crude materials resulting from this thermal treatment were chromatographed, thus resulting in the isolation of pure 2-substituted 4*H*-3,1-benzoxazin-4-ones **6** (Scheme 1).[30] Compounds **6** were obtained in acceptable global yields (40–50%) for the conversion **3** → **6**, three reaction steps in a one-pot process (Table 2).

The structural elucidation of the 4*H*-3,1-benzoxazin-4-ones **6** was achieved following their analytical and spectral data, and confirmed by the X-ray structure determination of a monocrystal of **6g** [R^1 = Cl; R^2 = Ph; Ar = 3,4-$(MeO)_2C_6H_3$].[31] The IR spectra of the 4*H*-3,1-benzoxazin-4-ones **6** exhibit strong absorptions in the region 1757–1772 cm^{-1} due to the vibration of the lactone carbonyl group, whereas the bands associated to the C=N double bond range between 1628 cm^{-1} and 1640 cm^{-1}. In the ^1H NMR spectra of compounds **6a**,**c**–**h** the two protons at the methylene carbon of the side chain resonate as a singlet at δ = 3.90–3.93 ppm. However, in the ^1H NMR spectrum of **6b** [R^1 = H; R^2 = Me; Ar = 4-MeC_6H_4] these two protons turned out to be diastereotopic, appearing at δ = 3.38 ppm and δ = 3.65 ppm with a geminal coupling constant *J* = 13.4 Hz, due to its stereogenic carbon atom. The proximity of the carbonyl group to the aromatic proton at C5 accounts for its chemical shift, δ = 8.08–8.15 ppm. The ^{13}C NMR spectra of the 2-substituted benzoxazinones **6** show the signal of the aliphatic quaternary carbon atom linked



Scheme 1 Preparation of 2-Substituted 4*H*-3,1-Benzoxazin-4-ones **6**

to C2 at δ = 49.7–60.8 ppm, and the signal of the methylene carbon at δ = 43.5–44.8 ppm. In these spectra the carbonyl carbon C4 appear at δ = 158.5–159.7 ppm, and carbon C2 fall in the range of δ = 163.5–165.7 ppm.

In the crystal structure of **6g** the 3,1-benzoxazin-4-one ring is planar, with a mean deviation of only 0.01 Å (Figure 1). The dihedral angles between the mean planes defined by the benzoxazinone nucleus and the phenyl rings are 99.4° (C11–C16), 89.4° (C21–C26), and 27.2° (C31–C36).

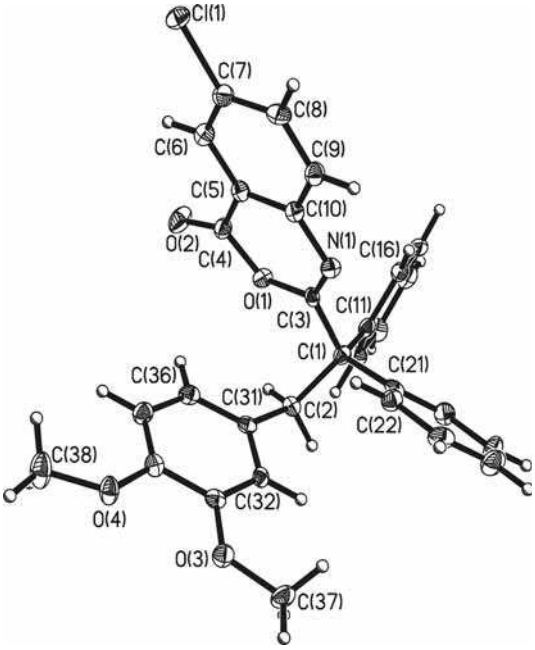


Figure 1 Molecular structure of **6g** with 50% probability ellipsoids, and the labeling scheme. Selected bond lengths (Å) and angles (°): C(1)–C(3) 1.509 (5), C(1)–C(21) 1.542 (5), C(1)–C(11) 1.548 (5), C(1)–C(2) 1.574 (4), O(1)–C(4) 1.385 (4), O(1)–C(3) 1.386 (4), N(1)–C(3) 1.268 (4), N(1)–C(10) 1.400 (4), C(3)–N(1)–C(10) 117.5 (3), C(4)–O(1)–C(3) 121.8 (3), C(3)–C(1)–C(21) 113.5 (3), C(3)–C(1)–C(11) 105.6 (3), C(21)–C(1)–C(11) 110.9 (3), C(3)–C(1)–C(2) 108.0 (3), C(21)–C(1)–C(2) 108.9 (3), C(11)–C(1)–C(2) 109.9 (3), N(1)–C(3)–O(1) 124.9 (3), C(31)–C(2)–C(1) 116.2 (3), N(1)–C(3)–C(1) 126.1 (3), O(1)–C(3)–C(1) 109.0 (3)

The conversion of ketenimines **5** into the 4*H*-3,1-benzoxazin-4-ones **6** involves the formation of a new carbon–oxygen bond, and the migration of the benzyl group from the oxygen atom of the ester function to the terminal carbon atom of the ketenimine fragment. Most probably, this migration occurs through one of the dipolar or radical-cage intermediates represented in Figure 2, although a precise mechanistic investigation of this process is out of the scope of the present work. The shift of benzyl groups from an oxygen atom to a carbon atom is quite rare, and, to our knowledge, only a few examples have been reported.[32]

Starting from 2-azidobenzoyl chloride (**1a**) and *N*-substituted benzyl amines we prepared ketenimines **7**, in which the amide function bears at least one benzyl group at the nitrogen atom. We reasoned that by thermal treatment these ketenimines, following a similar mechanistic sequence to that involved in the conversion **5** → **6**, could transform into quinazolin-4-ones **8** (Scheme 2). Unfortunately, when compounds **7** were heated at 200 °C for one hour in a sealed tube only very complex reaction mixtures were obtained.[29]

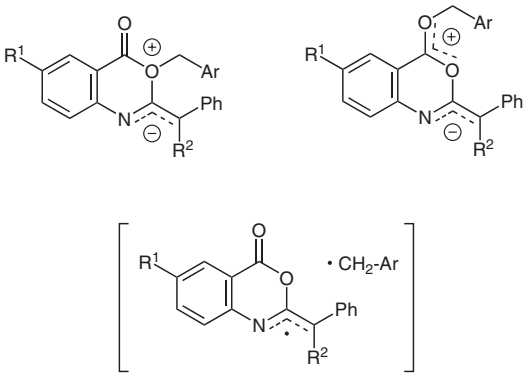
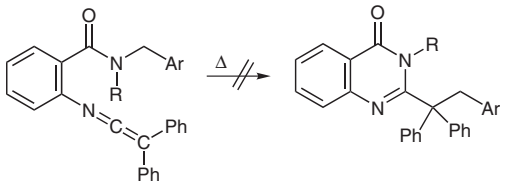


Figure 2 Putative intermediates in the transformation **5** → **6**



7a R = Me, Ar = 3-MeOC$_6$H$_4$ **8**

7b R = PhCH$_2$, Ar = Ph

Scheme 2 Attempted synthesis of quinazolin-4-ones **8**

In summary, the thermally induced intramolecular cyclization of the *N*-(2-benzyloxycarbonyl)phenyl ketenimines **5** provides new 2-substituted derivatives of the 4*H*-3,1-benzoxazin-4-one system, an heterocyclic nucleus of particular interest. Moreover, this process constitutes a new type of reaction in ketenimine chemistry, which involves the intramolecular migration of a benzyl group over its terminal carbon atom.

All melting points were determined on a Kofler hot-plate mp apparatus and are uncorrected. IR spectra were obtained as films or Nujol emulsions on a Nicolet Impact 400 spectrophotometer. NMR spectra were recorded on a Bruker Avance 300 (300 MHz and 75 MHz for ^{1}H and ^{13}C, respectively) or a Bruker Avance 400 spectrometer (400 MHz and 100 MHz for ^{1}H and ^{13}C, respectively), in $CDCl_3$ as solvent, and the chemical shifts are expressed in ppm relative to TMS at δ = 0.00 for ^{1}H and to $CDCl_3$ at δ = 77.1 for ^{13}C. Mass spectra were recorded on a Hewlett-Packard 5993C spectrometer or on a VG-Autospec spectrometer. Microanalyses were performed on a Carlo Erba EA-1108 instrument.

2-Azidobenzoyl chloride (**1a**),[33] 2-azido-5-chlorobenzoyl chloride (**1b**),[33] diphenylketene[34] and methylphenylketene[35] were prepared according to literature procedures.

The crystal and molecular structure of **6g** has been determined by X-ray diffraction studies. Crystal was mounted on glass fibre and transferred to the cold gas stream of the diffractometer Bruker Smart APEX. Data were recorded with Mo–Kα radiation (λ =

0.71073Å) in ω-scan mode. The structure was solved by the direct method and refined anisotropically on F^2 (program SHELXL-97, G.M. Sheldrick, University of Göttingen, Germany). Methyl groups were refined using rigid groups and other hydrogens were refined using a riding method.

Benzyl 2-Azidobenzoates 3; General Procedure

To a solution of 2-azidobenzoyl chloride (**1a**; 0.91 g, 5 mmol) or 2-azido-5-chlorobenzoyl chloride (**1b**; 1.08 g, 5 mmol) in anhyd CH_2Cl_2 (50 mL) were added DMAP (0.79 g, 6.5 mmol) and the corresponding benzyl alcohol **2** (5 mmol). The reaction mixture was stirred at r.t. for 5 h. Then *n*-hexane (50 mL) was added and the stirring was continued for 30 min. The precipitated solid was separated by filtration, and washed with *n*-hexane (3 × 15 mL). From the filtrate the solvent was removed under reduced pressure and the resulting material was purified by column chromatography.

4-Methylbenzyl 2-Azidobenzoate (3a)

Silica gel; hexane–Et_2O, 4:1. Yield: 1.1 g (82%); yellow oil.

IR (neat): 2124, 1724, 1597, 1580, 1520, 1489, 1452, 1373, 1301, 1253, 1129, 1074, 810, 755, 690 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.34 (s, 3 H), 5.30 (s, 2 H), 7.10–7.24 (m, 4 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 7.46–7.52 (m, 1 H), 7.86 (dd, *J* = 7.8, 1.6 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.2, 67.0, 119.9, 122.6 (s), 124.4, 128.5, 129.3, 131.9, 132.8 (s), 133.2, 138.1 (s), 140.2 (s), 165.0 (s).

MS (EI, 70 eV): *m*/*z* (%) = 105 (100), 267 (2) [M^+].

Anal. Calcd for $C_{15}H_{13}N_3O_2$: C, 67.40; H, 4.90; N, 15.72. Found: C, 67.21; H, 4.77; N, 15.90.

4-Methoxybenzyl 2-Azidobenzoate (3b)

Silica gel; hexane–Et_2O, 7:3. Yield: 1.06 g (75%); yellow oil.

IR (neat): 2126, 1725, 1616, 1597, 1518, 1490, 1450, 1302, 1243, 1179, 1124, 1073, 1037, 829, 752 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.79 (s, 3 H), 5.26 (s, 2 H), 6.88 (m, 2 H), 7.13 (t, *J* = 7.8 Hz, 1 H), 7.20 (d, *J* = 7.8 Hz, 1 H), 7.37–7.40 (m, 2 H), 7.46–7.50 (m, 1 H), 7.84 (dd, *J* = 7.8, 1.5 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.3, 66.8, 114.0, 119.8, 122.6 (s), 124.4, 127.9 (s), 130.2, 131.8, 133.2, 140.1 (s), 159.7 (s), 165.0 (s).

MS (EI, 70 eV): *m*/*z* (%) = 121 (100), 283 (4) [M^+].

Anal. Calcd for $C_{15}H_{13}N_3O_3$: C, 63.60; H, 4.63; N, 14.83. Found: C, 63.41; H, 4.57; N, 14.90.

3,4-Dimethoxybenzyl 2-Azidobenzoate (3c)

Silica gel; hexane–Et_2O, 2:3. Yield: 1.42 g (91%); yellow oil.

IR (neat): 2126, 1729, 1598, 1515, 1484, 1449, 1378, 1250, 1161, 1125, 1074, 1029, 946, 859, 809, 760 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.88 (s, 3 H), 3.90 (s, 3 H), 5.29 (s, 2 H), 6.85–6.88 (m, 1 H), 7.00–7.04 (m, 2 H), 7.16 (td, *J* = 8.1, 1.1 Hz, 1 H), 7.23 (dd, *J* = 8.1, 0.8 Hz, 1 H), 7.51 (ddd, *J* = 8.1, 7.5, 1.6 Hz, 1 H), 7.85 (dd, *J* = 7.5, 1.5 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.9, 56.0, 67.2, 111.1, 111.9, 119.9, 121.4, 122.7 (s), 124.5, 128.3 (s), 131.9, 133.3, 140.1 (s), 149.0 (s), 149.2 (s), 165.1 (s).

MS (EI, 70 eV): *m*/*z* (%) = 151 (100), 313 (29) [M^+].

Anal. Calcd for $C_{16}H_{15}N_3O_4$: C, 61.34; H, 4.83; N, 13.41. Found: C, 61.09; H, 4.67; N, 13.23.

4-Methylbenzyl 2-Azido-5-chlorobenzoate (3d)

Silica gel; hexane–Et_2O, 4:1.

Yield: 1.05 g (70%); colorless prisms; mp 71–73 °C (Et_2O–*n*-hexane).

IR (Nujol): 2130, 1722, 1480, 1310, 1294, 1241, 1227, 1135, 1119, 1073, 1055, 830, 806, 783, 720, 623 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.35 (s, 3 H), 5.29 (s, 2 H), 7.13 (d, *J* = 8.6 Hz, 1 H), 7.19 (d, *J* = 8.0 Hz, 2 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 7.44 (dd, *J* = 8.6, 2.5 Hz, 1 H), 7.82 (d, *J* = 2.5 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.2, 67.4, 121.3, 123.8 (s), 128.6, 129.4, 129.9 (s), 131.7, 132.4 (s), 133.1, 138.4 (s), 138.9 (s), 163.8 (s).

MS (EI, 70 eV): *m*/*z* (%) = 105 (100), 301 (4) [M^+], 303 (2) [M^+ + 2].

Anal. Calcd for $C_{15}H_{12}ClN_3O_2$: C, 59.71; H, 4.01; N, 13.93. Found: C, 59.65; H, 4.17; N, 13.90.

4-Methoxybenzyl 2-Azido-5-chlorobenzoate (3e)

Silica gel; hexane–Et_2O, 7:3. Yield: 1.27 g (80%); colorless prisms; mp 60–62 °C (Et_2O–*n*-hexane).

IR (Nujol): 2133, 1726, 1616, 1481, 1309, 1257, 1227, 1175, 1134, 1115, 1073, 1036, 829, 782, 715, 624 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.81 (s, 3 H), 5.27 (s, 2 H), 6.89–6.93 (m, 2 H), 7.14 (d, *J* = 8.6 Hz, 1 H), 7.37–7.40 (m, 2 H), 7.45 (dd, *J* = 8.6, 2.5 Hz, 1 H), 7.81 (d, *J* = 2.5 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.3, 67.3, 114.1, 121.3, 123.8 (s), 127.5 (s), 129.9 (s), 130.4, 131.6, 133.1, 138.8 (s), 159.9 (s), 163.9 (s).

MS (EI, 70 eV): *m*/*z* (%) = 121 (100), 317 (4) [M^+], 319 (2) [M^+ + 2].

Anal. Calcd for $C_{15}H_{12}ClN_3O_3$: C, 56.70; H, 3.81; N, 13.23. Found: C, 56.61; H, 3.77; N, 13.04.

3,4-Dimethoxybenzyl 2-Azido-5-chlorobenzoate (3f)

Silica gel; hexane–Et_2O, 1:1. Yield: 1.04 g (60%); colorless prisms; mp 81–83 °C (Et_2O–*n*-hexane).

IR (Nujol): 2134, 2101, 1717, 1524, 1311, 1271, 1219, 1169, 1142, 1113, 1023, 943, 859, 833, 805, 786 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.81 (s, 3 H), 3.82 (s, 3 H), 5.20 (s, 2 H), 6.79 (d, *J* = 8.0 Hz, 1 H), 6.91–6.96 (m, 2 H), 7.07 (d, *J* = 8.6 Hz, 1 H), 7.38 (dd, *J* = 8.6, 2.5 Hz, 1 H), 7.74 (d, *J* = 2.5 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.9, 67.5, 111.1, 112.0, 121.3, 121.6, 123.8 (s), 127.9 (s), 129.9 (s), 131.6, 133.1, 138.8 (s), 149.1 (s), 149.3 (s), 163.9 (s).

MS (EI, 70 eV): *m*/*z* (%) = 151 (100), 347 (9) [M^+], 349 (3) [M^+ + 2].

Anal. Calcd for $C_{16}H_{14}ClN_3O_4$: C, 55.26; H, 4.06; N, 12.08. Found: C, 55.02; H, 3.97; N, 11.94.

3,5-Dimethoxybenzyl 2-Azido-5-chlorobenzoate (3g)

Silica gel; hexane–Et_2O, 7:3. Yield: 1.36 g (78%); colorless prisms; mp 71–73 °C (Et_2O–*n*-hexane).

IR (Nujol): 2135, 2102, 1698, 1614, 1559, 1430, 1405, 1305, 1249, 1210, 1175, 1155, 1065, 1010, 835 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.79 (s, 6 H), 5.28 (s, 2 H), 6.44 (t, *J* = 2.3 Hz, 1 H), 6.59 (d, *J* = 2.3 Hz, 2 H), 7.17 (d, *J* = 8.6 Hz, 1 H), 7.47 (dd, *J* = 8.6, 2.5 Hz, 1 H), 7.85 (d, *J* = 2.5 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.4, 67.3, 100.4, 106.2, 121.3, 123.6 (s), 130.0 (s), 131.8, 133.3, 137.6 (s), 138.9 (s), 161.0 (s), 163.8 (s).

MS (EI, 70 eV): *m*/*z* (%) = 151 (100), 347 (9) [M^+], 349 (3) [M^+ + 2].

Anal. Calcd for $C_{16}H_{14}ClN_3O_4$: C, 55.26; H, 4.06; N, 12.08. Found: C, 55.09; H, 3.98; N, 11.89.

4*H*-3,1-Benzoxazin-4-ones 6; General Procedure

A solution of the corresponding benzyl 2-azidobenzoate **3** (2.5 mmol) in anhyd CH_2Cl_2 (10 mL) was introduced in a glass tube, and a solution of triphenylphosphane (0.65 g, 2.5 mmol) in the same solvent (6 mL) was added dropwise. The reaction mixture was stirred at r.t. under N_2 for 16 h. Then, methylphenylketene or diphenylketene (2.5 mmol) in CH_2Cl_2 (4 mL) was added. After stirring at r.t. for 10 min the solvent was removed to dryness under reduced pressure. The glass tube was sealed and the mixture containing the corresponding ketenimine **5** and triphenylphosphane oxide was heated at 200 °C for 1 h. After cooling at r.t. the crude mixture was dissolved in CH_2Cl_2 (20 mL) and transferred to a round bottom flask. Finally, the solvent was removed under reduced pressure and the resulting material was chromatographed. After removing the chromatography solvents under reduced pressure the 4*H*-3,1-benzoxazin-4-ones **6** were obtained as solids, that were triturated and dried under high vacuum a 50 °C for 24 h, and used as such for characterization.

As compounds **6c** and **6f** were isolated along with the corresponding 2-diphenylmethyl-4*H*-3,1-benzoxazin-4-one **9** (see ref.[30]) only their ^1H and ^{13}C NMR data are given.

2-[2-(4-Methylphenyl)-1,1-diphenylethyl]-4*H*-3,1-benzoxazin-4-one (6a)

Silica gel; hexane–Et_2O, 9:1. Yield: 0.47 g (45%).

IR (Nujol): 1760, 1631, 1607, 1515, 1495, 1263, 1172, 1046, 1002, 776, 699 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.18 (s, 3 H), 3.93 (s, 2 H), 6.62 (d, *J* = 7.9 Hz, 2 H), 6.79 (d, *J* = 7.9 Hz, 2 H), 7.21–7.34 (m, 10 H), 7.45 (td, *J* = 7.8, 1.1 Hz, 1 H), 7.65 (d, *J* = 8.1 Hz, 1 H), 7.75 (td, *J* = 8.1, 1.4 Hz, 1 H), 8.12 (dd, *J* = 7.8, 1.1 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.0, 44.0, 60.6 (s), 116.8 (s), 127.1, 127.2, 127.8, 128.1, 128.4, 128.5, 129.8, 131.2, 134.0 (s), 135.7 (s), 136.4, 142.5 (s), 146.2 (s), 159.6 (s), 163.5 (s).

MS (EI, 70 eV): *m*/*z* (%) = 105 (100), 417 (27) [M^+].

Anal. Calcd for $C_{29}H_{23}NO_2$: C, 83.43; H, 5.55; N, 3.35. Found: C, 83.21; H, 5.39; N, 3.14.

2-[1-Methyl-2-(4-methylphenyl)-1-phenylethyl]-4*H*-3,1-benzoxazin-4-one (6b)

Silica gel; hexane–Et_2O, 4:1. Yield: 0.38 g (43%).

IR (Nujol): 1757, 1633, 1608, 1475, 1447, 1323, 1262, 1165, 1111, 1067, 1039, 1007, 815, 778, 739, 698 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.67 (s, 3 H), 2.22 (s, 3 H), 3.38 (d, *J* = 13.4 Hz, 1 H), 3.65 (d, *J* = 13.4 Hz, 1 H), 6.78 (d, *J* = 7.9 Hz, 2 H), 6.92 (d, *J* = 7.9 Hz, 2 H), 7.18–7.35 (m, 5 H), 7.46 (td, *J* = 8.0, 1.1 Hz, 1 H), 7.62 (d, *J* = 7.9 Hz, 1 H), 7.75 (td, *J* = 7.9, 1.5 Hz, 1 H), 8.15 (dd, *J* = 8.0, 1.5 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0, 22.7, 44.8, 49.7 (s), 116.8 (s), 126.6, 127.0, 127.2, 128.3, 128.4, 128.6, 128.7, 130.5, 133.9 (s), 135.9 (s), 136.4, 143.3 (s), 146.1 (s), 159.7 (s), 165.7 (s).

MS (EI, 70 eV): *m*/*z* (%) = 105 (100), 355 (14) [M^+].

Anal. Calcd for $C_{24}H_{21}NO_2$: C, 81.10; H, 5.90; N, 3.94. Found: C, 81.29; H, 5.79; N, 3.84.

2-[2-(4-Methoxyphenyl)-1,1-diphenylethyl]-4*H*-3,1-benzoxazin-4-one (6c)

Silica gel; hexane–Et_2O, 7:3. Yield: 0.44 g (41%).

^1H NMR (300 MHz, $CDCl_3$): δ = 3.63 (s, 3 H), 3.92 (s, 2 H), 6.52 (d, *J* = 8.6 Hz, 2 H), 6.65 (d, *J* = 8.6 Hz, 2 H), 7.17–7.33 (m, 10 H), 7.40 (t, *J* = 7.8 Hz, 1 H), 7.63 (d, *J* = 8.1 Hz, 1 H), 7.73 (t, *J* = 8.1 Hz, 1 H), 8.08 (d, *J* = 7.8 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 43.5, 55.0, 60.7 (s), 112.7, 116.7 (s), 127.0, 127.1, 127.7, 128.7, 129.0, 129.7, 132.2, 136.4, 138.5 (s), 142.5 (s), 146.0 (s), 158.0 (s), 159.4 (s), 163.5 (s).

2-[2-(3,4-Dimethoxyphenyl)-1,1-diphenylethyl]-4*H*-3,1-benzoxazin-4-one (6d)

Silica gel; hexane–Et_2O, 2:3. Yield: 0.49 g (42%).

IR (Nujol): 1759, 1636, 1608, 1516, 1496, 1445, 1421, 1283, 1263, 1159, 1140, 1029, 1005, 777, 701 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.46 (s, 3 H), 3.76 (s, 3 H), 3.92 (s, 2 H), 6.06 (s, 1 H), 6.51–6.56 (m, 2 H), 7.25–7.32 (m, 10 H), 7.49 (t, *J* = 7.7 Hz, 1 H), 7.76 (d, *J* = 8.0 Hz, 1 H), 7.79 (td, *J* = 8.0, 1.3 Hz, 1 H), 8.14 (d, *J* = 8.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 43.9, 55.3, 55.7, 60.7 (s), 110.2, 114.5, 116.8 (s), 123.4, 127.1, 127.9, 128.4, 128.6, 129.5 (s), 129.8, 136.5, 142.6 (s), 146.2 (s), 147.4 (s), 147.6 (s), 159.6 (s), 163.5 (s).

MS (EI, 70 eV): *m*/*z* (%) = 151 (100), 463 (3) [M^+].

Anal. Calcd for $C_{30}H_{25}NO_4$: C, 77.73; H, 5.44; N, 3.02. Found: C, 77.55; H, 5.29; N, 3.24.

6-Chloro-2-[2-(4-methylphenyl)-1,1-diphenylethyl]-4*H*-3,1-benzoxazin-4-one (6e)

Silica gel; hexane–Et_2O, 9:1. Yield: 0.56 g (50%).

IR (Nujol): 1772, 1628, 1603, 1514, 1495, 1472, 1312, 1249, 1156, 1047, 1033, 875, 838, 771, 716, 702 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.19 (s, 3 H), 3.91 (s, 2 H), 6.59 (d, *J* = 8.0 Hz, 2 H), 6.79 (d, *J* = 8.0 Hz, 2 H), 7.22–7.28 (m, 10 H), 7.60 (d, *J* = 8.6 Hz, 1 H), 7.71 (dd, *J* = 8.6, 2.4 Hz, 1 H), 8.08 (d, *J* = 2.4 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.0, 44.0, 60.7 (s), 117.9 (s), 127.2, 127.8, 127.9, 128.2, 128.8, 129.7, 131.2, 133.8 (s), 134.2 (s), 135.9 (s), 136.7, 142.3 (s), 144.6 (s), 158.5 (s), 163.9 (s).

MS (EI, 70 eV): *m*/*z* (%) = 105 (100), 451 (13) [M^+], 453 (4) [M^+ + 2].

Anal. Calcd for $C_{29}H_{22}ClNO_2$: C, 77.07; H, 4.91; N, 3.10. Found: C, 76.94; H, 4.78; N, 3.04.

6-Chloro-2-[2-(4-methoxyphenyl)-1,1-diphenylethyl]-4*H*-3,1-benzoxazin-4-one (6f)

Silica gel; hexane–Et_2O, 9:1. Yield: 0.47 g (40%).

^1H NMR (300 MHz, $CDCl_3$): δ = 3.70 (s, 3 H), 3.93 (s, 2 H), 6.54–6.58 (m, 2 H), 6.63–6.67 (m, 2 H), 7.26–7.33 (m, 10 H), 7.64 (d, *J* = 8.6 Hz, 1 H), 7.74 (dd, *J* = 8.6, 2.4 Hz, 1 H), 8.11 (d, *J* = 2.4 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 43.5, 55.1, 60.8 (s), 112.8, 117.9 (s), 127.2, 127.9, 128.8, 129.0, 129.7, 132.2, 134.3 (s), 136.7, 138.3 (s), 142.3 (s), 144.6 (s), 158.1 (s), 158.5 (s), 163.9 (s).

6-Chloro-2-[2-(3,4-dimethoxyphenyl)-1,1-diphenylethyl]-4*H*-3,1-benzoxazin-4-one (6g)

Silica gel; hexane–Et_2O, 9:1. Yield: 0.53 g (43%).

IR (Nujol): 1765, 1640, 1608, 1520, 1424, 1314, 1264, 1238, 1143, 1027, 1019, 877, 857, 812, 768, 708 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.45 (s, 3 H), 3.76 (s, 3 H), 3.90 (s, 2 H), 6.00 (d, *J* = 1.7 Hz, 1 H), 6.51 (dd, *J* = 8.3, 1.7 Hz, 1 H), 6.55 (d, *J* = 8.3 Hz, 1 H), 7.23–7.32 (m, 10 H), 7.60 (d, *J* = 8.6 Hz, 1 H), 7.72 (dd, *J* = 8.6, 2.4 Hz, 1 H), 8.09 (d, *J* = 2.4 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 43.8, 55.3, 55.7, 60.7 (s), 110.2, 114.5, 117.9 (s), 123.3, 127.2, 127.8, 127.9, 128.6, 129.3 (s), 129.8, 134.3 (s), 136.7, 142.3 (s), 144.6 (s), 147.5 (s), 147.6 (s), 158.5 (s), 163.9 (s).

MS (EI, 70 eV): *m*/*z* (%) = 151 (100), 497 (4) [M^+], 499 (2) [M^+ + 2].

Anal. Calcd for $C_{30}H_{24}ClNO_4$: C, 72.36; H, 4.86; N, 2.81. Found: C, 73.21; H, 4.69; N, 2.77.

Crystal Data for 6g

$C_{30}H_{24}ClNO_4$, M = 497.95, Monoclinic, space group *P*2(1)/*c*, *a* = 9.1353 (6), *b* = 17.3153 (11), *c* = 15.5769 (11) Å, β = 98.496 (2), *V* = 2436.9 (3) Å^3, *Z* = 4, λ(Mo – Kα) = 0.71073 Å, T = 100 K, μ = 0.19 mm^{-1}, 26253 reflections measured, 4995 unique (R_{int} = 0.0738) used in all calculations. The final *R*1 was 0086 [I > 2α (I)] and *wR*2 was 0.144 (all data).

6-Chloro-2-[2-(3,5-dimethoxyphenyl)-1,1-diphenylethyl]-4*H*-3,1-benzoxazin-4-one (6h)

Silica gel; hexane–Et_2O, 7:3. Yield: 0.5 g (40%).

IR (Nujol): 1764, 1628, 1599, 1471, 1380, 1314, 1206, 1153, 1068, 838, 776, 705 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.48 (s, 6 H), 3.90 (s, 2 H), 5.91 (d, *J* = 2.3 Hz, 2 H), 6.18 (t, *J* = 2.3 Hz, 1 H), 7.24–7.34 (m, 10 H), 7.62 (d, *J* = 8.6 Hz, 1 H), 7.73 (dd, *J* = 8.6, 2.4 Hz, 1 H), 8.09 (d, *J* = 2.4 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 44.5, 55.0, 60.7 (s), 99.3, 109.1, 117.9 (s), 127.3, 127.8, 127.9, 128.7, 129.7, 134.3 (s), 136.8, 139.1 (s), 142.3 (s), 144.6 (s), 158.5 (s), 159.7 (s), 163.8 (s).

MS (EI, 70 eV): *m*/*z* (%) = 151 (100), 497 (13) [M^+], 499 (4) [M^+ + 2].

Anal. Calcd for $C_{30}H_{24}ClNO_4$: C, 72.36; H, 4.86; N, 2.81. Found: C, 72.09; H, 4.71; N, 2.68.

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(29) Ketenimines **5** and **7** remained unaltered when heated in boiling toluene or boiling *ortho*-xylene.
(30) In the thermal treatment of the *N*-(2-benzyloxycarbonyl)phenyl ketenimines **5** small amounts of the corresponding 4*H*-3,1-benzoxazin-4-ones **9** (Figure 3) were always formed (8–13%).

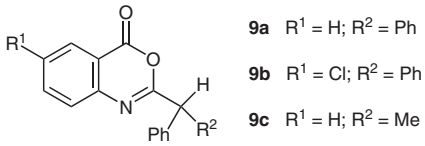

Figure 3

Probably, compounds **9** resulted from the hydrolysis of the ketenimine function in the *N*-(2-benzyloxycarbonyl)phenyl ketenimines **5** to yield the corresponding amides, followed by intramolecular nucleophilic displacement of the benzyloxy group from the ester group by the carbonyl oxygen of the amide function. We tried very hard to exclude water from the reaction mixtures, but probably we did not succeed as the results were invariable, and small amounts of benzoxazinones **9** were always formed.
Compounds **9a** (R^1 = H) and **9b** (R^1 = Cl) could not be separated from the 4*H*-3,1-benzoxazin-4-ones **6c** [R^1 = H; R^2 = Ph; Ar = 4-$MeOC_6H_4$] and **6f** [R^1 = Cl; R^2 = Ph; Ar = 4-$MeOC_6H_3$], respectively.

(31) CCDC 264507 contains the supplementary crystallographic data for **6g**. The data can be obtained free of charge via *www.ccdc.cam.ac.uk/conts/retrieving.html* (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; e-mail:deposit@ccdc.cam.ac.uk).
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