

Synthesis and chemical reactivity of methoxycarbonyl-1,3-dioxinyl(pivaloyl)ketene—a persistent α -oxoketene

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Flash vacuum pyrolysis of an equimolar mixture of 4-pivaloyl- and 4-methoxycarbonyl-5-*tert*-butylfuran-2,3-dione affords the new and remarkably stable α -oxoketene **6** as the result of an unusual dimerization of the primarily formed monomeric α -oxoketenes **1** and **3**, respectively. [2 + 2] Cycloaddition reactions of **6** and dialkylcarbodiimides furnish functionalized imino- β -lactams **7**, while reaction with nucleophiles results in complete degradation of **6** into smaller fragments. Structural confirmation of **6** and **7** is mainly based upon single crystal X-ray analyses.

Introduction

Flash Vacuum Pyrolysis (FVP) of suitably substituted furan-2,3-diones has been found to be an efficient method of generating α -oxoketenes,¹ highly reactive molecules which usually cannot be isolated or even observed under ordinary reaction conditions. However, they may be stabilized both electronically and sterically; in particular, the bulky *tert*-butyl group plays an important role in this context. Thus, dipivaloylketene **1**² as well as its dimer, 2-[3,3-dimethyl-2-oxo-1-(oxomethylene)butyl]-2,6-di-*tert*-butyl-5-pivaloyl-1,3-dioxin-4-one **2** are remarkably stable and have been prepared on a preparative scale as neat compounds.³ This also holds for methoxycarbonyl(pivaloyl)ketene **3**.⁴

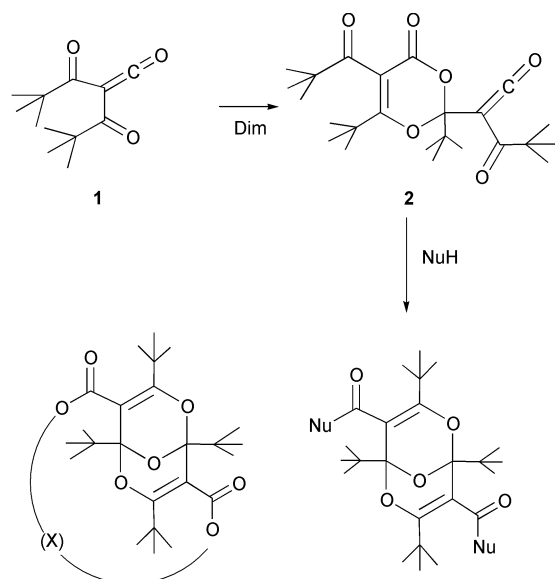
The dimeric oxoketene **2**, when reacted with several NH- or OH-nucleophiles, is converted into mono- or bifunctionalized 'bridged bisdioxines' (see Chart 1), which are rather rare hetero-

type thus generating novel highly lipophilic host-molecules.⁶ Unfortunately, because of the strong steric hindrance exerted by the bulky tertiary butyl groups the ability of such molecules to undergo host-guest interactions, *e.g.* towards metal ions is rather low.⁶ In order to enhance their potential complexation properties a change in the substitution pattern of the spacer molecule was envisaged by changing the substitution pattern of the corresponding α -oxoketene itself.

Results and discussion

Methoxycarbonyl(pivaloyl)ketene **3** was generated by FVP of the corresponding furan-2,3-dione.⁴ This ketene slowly dimerized at room temperature to afford the dioxinone derivative **4**⁴ *via* a rather unusual acylketene dimerization.³ The desired dimeric α -oxoketene **5** could not be obtained, and therefore a bridged bisdioxine skeleton analogous to that formed from dimer **2** (Chart 1) was unobtainable.

In continuation of these experiments we then tried to prepare a 'mixed' dimeric α -oxoketene by combining the two monomeric α -oxoketenes **1** and **3**, generated separately *via* FVP of the corresponding precursors. After mixing the oxoketenes **1** and **3**, even with variation of their molar ratio, in no case could the desired mixed dimeric α -oxoketene, *e.g.* **6**, be observed. Instead, either the known dimer **2** or products resulting from hydrolysis of the monomeric oxoketenes could be detected chromatographically. Since the conditions for FVP of both furandiones were very similar (sublimation temperature: 60–70 °C; pyrolysis temperature: 400 °C; vacuum: 10⁻³ mbar; pyrolysis time 3.5–4 hours) we then pyrolysed a nearly equimolar mixture (slight excess of the methoxycarbonyl substituted derivative) of the two furandiones *simultaneously*. The result was that, in addition to minor amounts of dimers **2** and **4** (detected by TLC), the new dimeric α -oxoketene **6** could be obtained in 30–40% yield after warm-up of the material collected at the cold-finger. Obviously, when generated simultaneously, the two oxoketenes **1** and **3** are trapped in a highly intimate mixture which during warm-up makes formation of the mixed dimer **6** more likely than homo-dimers **2** or **4**, at least from a statistical point of view. Furthermore, it cannot be excluded that some hetero-dimerization may already occur in the gas phase, *i.e.* in the cooler regions of the pyrolysis tube. First evidence for the presence of a ketene moiety in **6** came from the strong IR-absorption band at 2130 cm⁻¹. From 2D-NMR spectra and NOE-experiments [the *t*-Bu signal at δ 1.20 ppm collapsed upon



X = alkyl or PEG-chains

Chart 1

cyclic systems exhibiting axial chirality.⁵ Due to their specific geometry the bis-carboxylic acid derivatives might serve as novel spacer units in macrocyclic systems of the crown ether

irradiation of the OMe signal (δ 3.85 ppm)], the position of the methoxycarbonyl substituent at C-5 of the dioxinone ring as well as the presence of three *tert*-butyl groups in relation to one *O*-methyl could be confirmed. The spectroscopic and analytical data already enabled us to distinguish between the four possible dimerization products of oxoketenes **1** and **3**; however, the final confirmation came from a single crystal X-ray diffraction study of **6** (Fig. 1).

Crystal structure of **6**

A stereoscopic ORTEP⁷ plot of compound **6** is shown in Fig. 1. As in 2-[3,3-dimethyl-2-oxo-1-(oxomethylene)butyl]-2,6-di-*tert*-butyl-5-pivaloyl-1,3-dioxin-4-one (**2**),² the ketene group is nearly coplanar to the α -keto group [torsion angle C10–C11–C12–O12 $-176.3(2)^\circ$]. A comparison of the two structures (see Fig. 2) shows that the 3,3-dimethyl-2-oxo-1-(oxomethylene)butyl group and the *tert*-butyl group at C6 are rotated *ca.* 180° about the C2–C11 bond and the C6–C60 bonds, respectively, but that the *tert*-butyl group at C2 retains its orientation. As in **2** the ketene group is sterically well protected resulting in the high stability of compound **6**. The bonding parameters of the ketene group [C=C, 1.328(3) Å, C=O, 1.147(3) Å] agree well with those (only 3 hits) found in the literature^{2,8,9} via the Cambridge Structural Database.¹⁰ The 1,3-dioxin-4-one ring assumes an envelope form [deviations from the least squares plane: O1, $-0.023(4)$; O3 0.007(5); C4 0.008(5); C5 $-0.031(5)$; C6 0.039(5); C2 $-0.569(5)$ Å].

Cycloaddition reactions of **6**

α -Oxoketenes in general show a pronounced tendency to form

[4 + 2] Diels–Alder adducts when trapped with dienophiles.^{1,3} Accordingly, this was also found with the monomeric α -oxoketenes **1**^{3,11} and **3**.⁴ Carbodiimides are particularly reactive and lead to 1,3-oxazinone derivatives.^{12–14} The dimeric α -oxoketenes **2** and **6**, respectively, are more reluctant to undergo cycloaddition reactions with dienophiles: the main product from reaction of **2** with carbodiimides are functionalised β -lactams resulting from [2 + 2] processes instead of the usual [4 + 2] reactions.³ The reaction of dimeric oxoketene **6** and carbodiimides follows exactly the same reaction pathway: again the β -lactam derivatives **7a,b** were isolated in low to moderate yields (15–35%) as the main reaction products (see Scheme 1). Note that the [2 + 2] addition (*rac*-**6** + carbodiimide \rightarrow **7**) generates two neighbouring asymmetric carbon atoms and therefore may lead to diastereomers, while, due to the C=N double bond, *E/Z* isomers should also exist. This was first made evident from the splitting of signals in the ¹H and ¹³C NMR spectra of **7** (see the Experimental section) and nicely confirmed by a single crystal X-ray diffraction analysis of **7b**, which indicated the presence of a conglomerate of crystals containing both diastereomers, the *meso-R,S*-form as well as the *R,R(S,S)* racemate. In the case of di-(*p*-tolyl)carbodiimide, the [4 + 2] adduct **8** was isolated in low yield (9%) after separation from polymeric material. Obviously, **6** underwent cycloreversion reactions to the monomeric oxoketenes **1** and **3** under the reaction conditions. The more stable dipivaloylketene **1** was ultimately trapped by the carbodiimide to afford the oxazinone derivative **8** following the usual behaviour of monomeric α -oxoketenes.^{3,4}

The reason for the different behaviour in the cycloaddition reactions of the monomeric oxoketenes **1** and **3** compared with

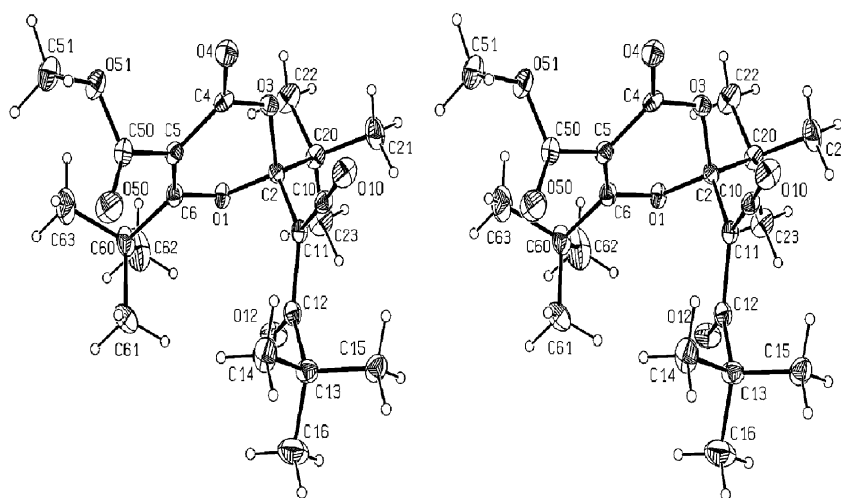


Fig. 1 Stereoscopic ORTEP⁷ plot of **6** showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level.

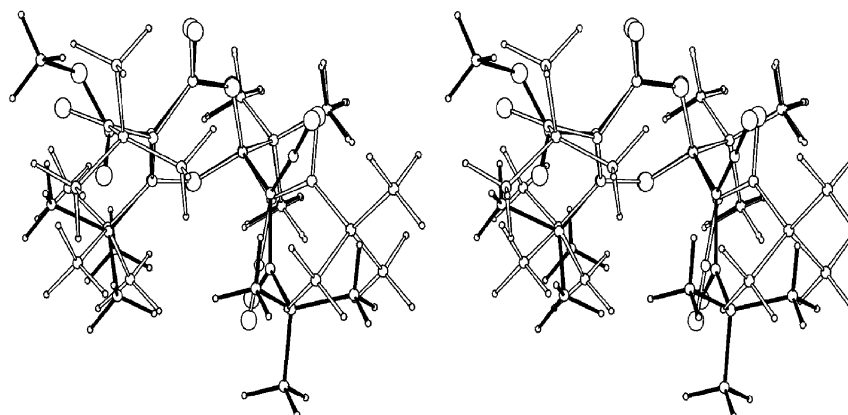


Fig. 2 Stereoscopic ORTEP⁷ plot showing a comparison of the molecules of **6** (filled bonds) and of **2** (empty bonds). A least-squares fit was performed for the equivalent atomic positions of the 1,3-dioxinone ring and the five atoms bonded to it. The atoms are drawn with arbitrary radii.

spectrometer. Elemental analyses were determined on a Carlo Erba Elemental Analyzer 1106 apparatus. Preparative-scale FVP was performed with the aid of a Büchi-GKR-51 sublimation unit and an AHT pyrolysis oven. TLC conditions: silica gel plates (Merck); eluant dichloromethane.

Dipivaloylmethane, methyl 4,4-dimethyl-3-oxopentanoate and oxalyl chloride as starting materials as well as *N,N'*-diisopropylcarbodiimide and *N,N'*-di-(4-tolyl)carbodiimide as reagents were purchased from Sigma-Aldrich. 5-*tert*-Butyl-4-pivaloylfuran-2,3-dione³ and 5-*tert*-butyl-4-methoxycarbonylfuran-2,3-dione⁴ as well as the α -oxoketenes **1**,² **2**^{2,3} and **3**⁴ were prepared according to published procedures.

2-[3,3-Dimethyl-2-oxo-1-(oxomethylene)butyl]-2,6-di-*tert*-butyl-5-methoxycarbonyl-1,3-dioxin-4-one (**6**)

An intimate mixture of dry 5-*tert*-butyl-4-pivaloylfuran-2,3-dione³ (1.5 g, 0.63 mmol) and dry 5-*tert*-butyl-4-methoxycarbonylfuran-2,3-dione⁴ (1.5 g, 0.76 mmol) was placed in the sublimation tube of the FVP unit, connected to the pyrolysis tube and the whole system evacuated to approximately 5×10^{-3} mbar. At 60–70 °C the two furandiones began to sublime into the pyrolysis tube which was held at 400 °C. The two α -oxoketenes **1** and **3** formed were trapped on the cold-finger which was cooled by liquid nitrogen. When the pyrolysis was

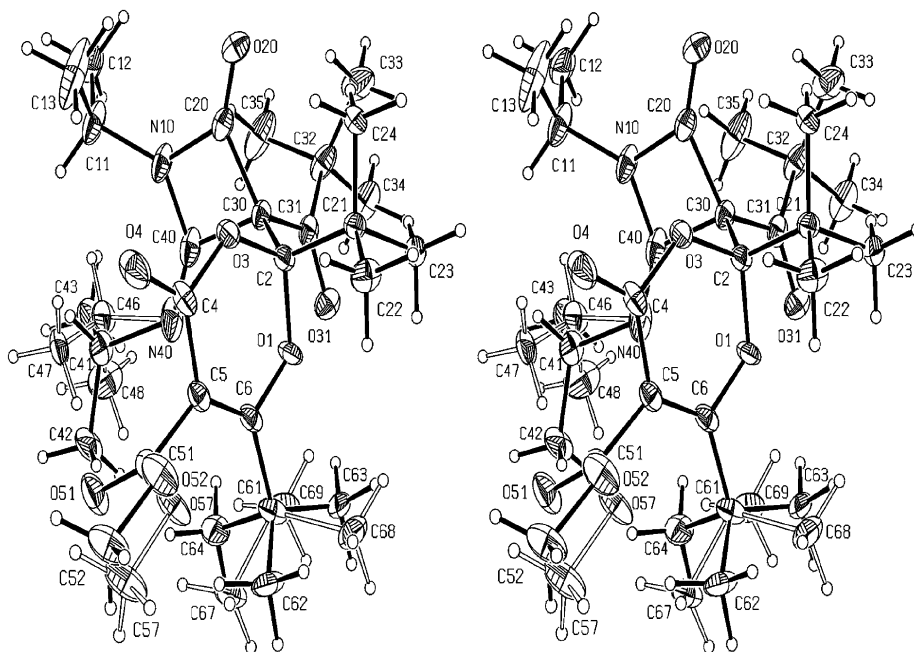


Fig. 3 Stereoscopic ORTEP⁷ plot of **A** showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The less occupied orientations of the disordered groups are drawn with empty bonds.

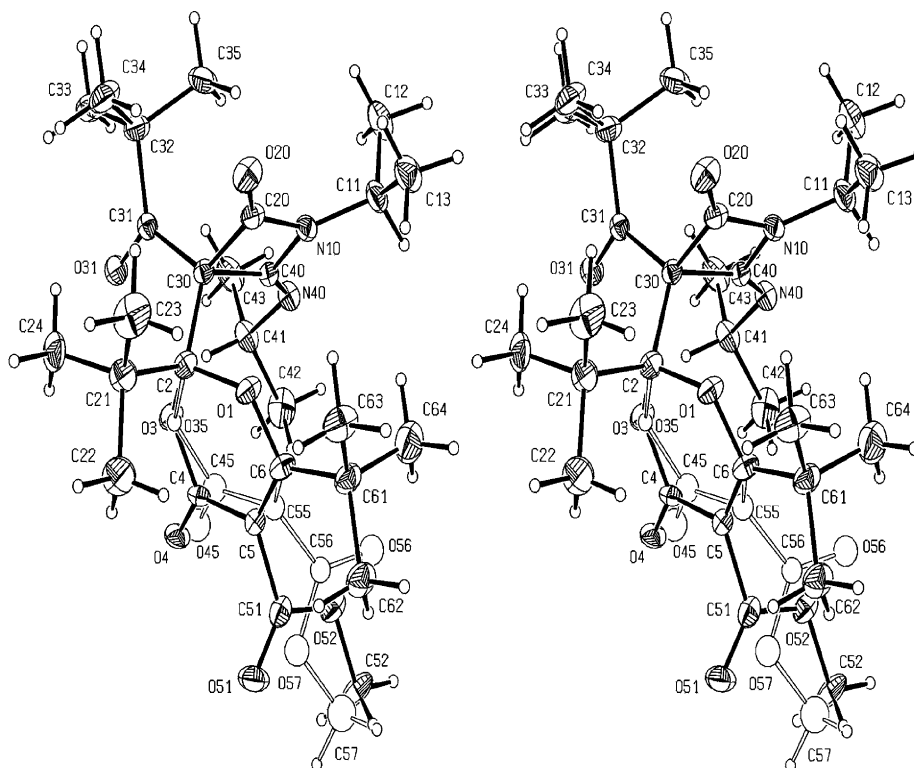
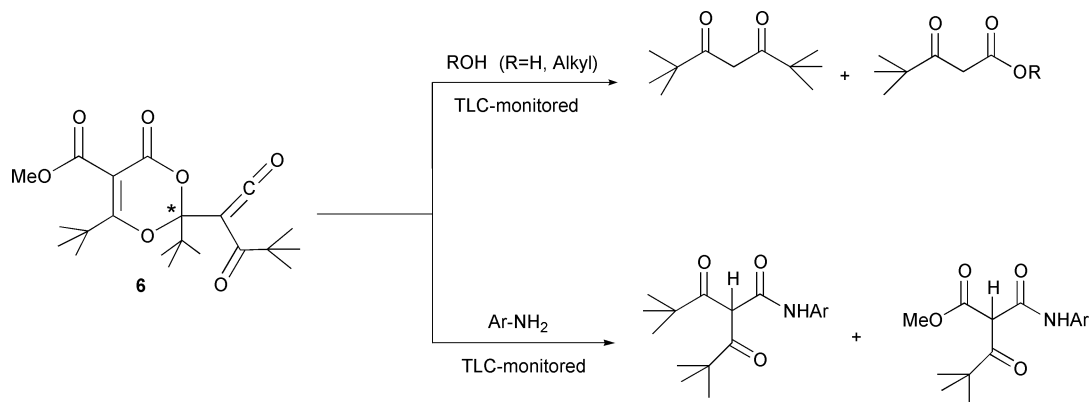


Fig. 4 Stereoscopic ORTEP⁷ plot of **B** showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The less occupied orientation of the isotropically refined disordered group is drawn with empty bonds.



Scheme 2

finished, the cold-finger was warmed to room temperature and the oily liquid thus obtained was allowed to stand for 2 days until it had turned into a crystalline pulp, which indicated formation of the dimeric oxoketene **6**. The crude product was then triturated with ice-cold *n*-hexane (2 ml) and after suction filtration the material was recrystallized from *n*-hexane to afford neat **6** as colourless crystals (1 g, 40%); mp 80 °C; ν_{\max} (KBr) 3060–2840, 2130, 1741, 1723, 1666, 1600 cm^{-1} ; δ_{H} (360 MHz; CDCl_3) 3.82 (3H, s, OMe), 1.25 (9H, s, *t*-Bu), 1.20 (9H, s, *t*-Bu), 1.12 (9H, s, *t*-Bu); δ_{C} (90.5 MHz, CDCl_3) 197.3 (*t*-BuC=O), 189.4 (C=C=O), 176.7 (C-6), 165.0 (MeOC=O), 158.6 (C-4), 108.6 (C-2), 103.5 (C-5), 52.7 (OCH₃), 49.1 (C=C=O), 46.0, 43.1, 38.4 [C(Me)₃], 27.9, 27.1, 24.7 [C(CH₃)₃]; MS (APCI) m/z 395.3 ($\text{M}^+ + 1$, 50%), 311.3 (15%), 211.1 (100%), 185.3 (12%). (Calc. for $\text{C}_{21}\text{H}_{30}\text{O}_7$: C, 63.94; H, 7.66. Found: C, 63.94; H, 7.86%).

Reaction of dimeric oxoketene **6** with carbodiimides—general procedure

A mixture of neat **6** (300 mg, 0.76 mmol) and the corresponding carbodiimide (1.52 mmol) was warmed to 60 °C (25 °C for dimethylcarbodiimide) and kept at this temperature for 12 h [60 h for di(*p*-tolyl)carbodiimide] with stirring in a rigorously anhydrous atmosphere. The progress of the reaction was carefully monitored by TLC (solvent dichloromethane). After being cooled to rt the crude products were triturated with cold *n*-hexane (in case of **8** refluxed in *n*-hexane for 5 min) to afford the pure compounds.

2-[1-Methyl-4-(methylimino)-2-oxo-3-pivaloylazetid-3-yl]-2,6-di-*tert*-butyl-5-methoxycarbonyl-1,3-dioxin-4-one (**7a**)

Freshly prepared dimethylcarbodiimide^{16,17} (0.107 g, 1.52 mmol) and **6** were reacted at rt¹⁶ for 16 h to give **7a** (0.11 g, 15%); mp 112 °C; ν_{\max} 3040–2840, 1830w, 1740s, 1715s, 1618w cm^{-1} ; δ_{H} (360 MHz, CDCl_3) 3.80 (3H, s, OMe), 3.35, 3.28, 3.15, 2.92 (6H, 4s, NMe), 1.0–1.35 (27H, *t*-Bu); δ_{C} (90.5 MHz, CDCl_3) 203.8/201.9 (*t*-BuC=O), 174.5/173.6 (C-6), 165.4/165.1 (C-4), 164.9/164.6 (MeOC=O), 156.3/156.1 (NC=O), 145.1/143.5 (C=NMe), 111.9/111.2 (C-5), 100.3/99.7 (C-2), 84.7, 84.3 (CC=NMe), 52.8/52.7 (OCH₃), 48.6/48.0, 45.2/43.9 (NCH₃), 38.3/38.2, 35.7/35.1, 30.1 [C(Me)₃], 27.9–24.9 (CCH₃)₃ (Calc. for $\text{C}_{24}\text{H}_{36}\text{N}_2\text{O}_7$: C, 62.06; H, 7.76; N, 6.03. Found: C, 61.64; H, 8.04; N, 6.38%).

2-[1-Isopropyl-4-(isopropylimino)-2-oxo-3-pivaloylazetid-3-yl]-2,6-di-*tert*-butyl-5-methoxycarbonyl-1,3-dioxin-4-one (**7b**)

From diisopropylcarbodiimide (0.191 g, 1.52 mmol) and **6** after 12 h the yield of **7b** was 0.275 (35%); mp 121 °C; ν_{\max} 3060–2840, 1810w, 1750s, 1710s, 1685, 1620 cm^{-1} ; δ_{H} (360 MHz, CDCl_3) *E/Z* isomers (*E*:*Z* ≈ 5:1) *E*-isomer: 4.05 (2H, sept., *J* = 6.5 Hz), 3.78 (3H, s, OMe), *Z*-isomer: 4.42, 3.90 (2H, sept., *J* = 6.5 Hz), 3.84 (3H, s, OMe) 1.65–0.95 (39H, m, CH₃); δ_{C} (90.5 MHz, CDCl_3) 203.9, 203.2, 202.9, 200.9 (*t*-BuC=O), 176.7,

175.7, 175.5, 174.5 (C-6), 165.9, 165.7, 165.6, 165.5, 165.1, 164.9 (C-4, MeOC=O), 157.6, 157.3, 156.9 (NC=O), 140.9, 140.8, 140.3 (C=N*i*Pr), 113.0, 112.5, 112.2, 112.0 (C-5), 101.6, 100.9, 100.0, 99.1 (C-2), 84.2, 82.4, 82.3 (CC=N), 52.7, 52.5 (OCH₃), 49.9–37.9 [14 signals, NCH(Me)₂, C(Me)₃], 28.0–19.3 (17 signals, CH₃); MS (APCI) m/z 521.5 ($\text{M}^+ + 1$, 100%), 337.3 (65%), 235.3 (8%), 127.6 (5%) (Calc. for $\text{C}_{28}\text{H}_{44}\text{N}_2\text{O}_7$: C, 64.63; H, 8.72; N, 5.41. Found: C, 64.67; H, 8.90; N, 5.47%).

6-*tert*-Butyl-3-(4-methylphenyl)-2-(4-methylphenylimino)-5-pivaloyl-1,3-oxazin-4-one (**8**)

The crude product from **6** and di(*p*-tolyl)carbodiimide was refluxed in 2 ml of *n*-hexane twice for 5 min and filtered from insoluble material. From the hexane solution, 30 mg (9%) of pure **8** crystallized upon cooling; mp 178–180 °C; ν_{\max} 3040–2840, 1700w, 1660s, 1600 cm^{-1} ; δ_{H} (360 MHz, CDCl_3) 1.11 (9H, s), 1.30 (9H, s), 2.28 (3H, s), 2.37 (3H, s), 6.75–7.30 (8H, m); δ_{C} (90.5 MHz, CDCl_3) 201.7 (*t*-BuC=O), 168.2 (C-6), 160.6 (C-4), 142.1 (C-2), 141.8, 138.9, 132.7, 132.2 (quarternary aryl-C), 130.3, 129.1, 128.1, 122.1 (aryl-C), 113.1 (C-5), 45.2, 37.7 [C(Me)₃], 28.5, 28.0 [C(CH₃)₃], 21.3, 20.9 (CH₃) (Calc. for $\text{C}_{27}\text{H}_{32}\text{N}_2\text{O}_3$: C, 75.00; H, 7.40; N, 6.48. Found: C, 74.75; H, 7.38; N, 6.37%).

X-Ray diffraction data of **6**†

All the measurements were performed using graphite-monochromatized Mo-K α radiation at 95 K: $\text{C}_{21}\text{H}_{30}\text{O}_7$, M_r 394.45, orthorhombic, space group $P2_12_12_1$, $a = 9.975(2)$ Å, $b = 11.266(2)$ Å, $c = 19.208(4)$ Å, $V = 2158.6(7)$ Å³, $Z = 4$, $d_{\text{calc}} = 1.214$ g cm^{-3} , $\mu = 0.090$ mm⁻¹. A total of 3197 reflections were collected ($2\theta_{\text{max}} = 52^\circ$), of which 2741 were unique ($R_{\text{int}} = 0.0317$), with 2477 having $I > 2\sigma(I)$. The structure was solved by direct methods (SHELXS-97)¹⁸ and refined by full-matrix least-squares techniques against F^2 (SHELXL-97).¹⁹ The non-hydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were refined with common isotropic displacement parameters for the H-atoms of the same methyl group and idealized geometry with C–H distances of 0.98 Å. Due to the absence of heavier elements the absolute structure of the chiral molecules could not be determined reliably. For 264 parameters final *R* indices of $R = 0.0359$ and $wR_2 = 0.0850$ (GOF = 1.052) were obtained. The largest peak in a difference Fourier map was 0.159 e Å⁻³. See Table 1 for selected bond lengths and angles.

Single-crystal X-ray diffraction analyses of **7b** (molecules A and B)†

All the measurements were recorded using graphite-monochromatized Mo-K α radiation at 90 K. The structures

† CCDC reference numbers 175718–175720. See <http://www.rsc.org/suppdata/pl/b1/b111143d/> for crystallographic files in .cif or other electronic format.

Table 1 Selected bond lengths (Å) and angles (°) for **6**

O(1)–C(2)	1.427(2)
C(2)–O(3)	1.431(2)
O(3)–C(4)	1.373(2)
C(4)–C(5)	1.456(3)
C(5)–C(6)	1.354(3)
O(1)–C(6)	1.349(2)
C(2)–C(11)	1.541(3)
C(11)–C(10)	1.328(3)
C(10)–O(10)	1.147(3)
C(11)–C(12)	1.484(3)
C(12)–O(12)	1.215(3)
C(12)–C(13)	1.539(3)
C(2)–C(20)	1.542(3)
C(4)–O(4)	1.200(2)
C(5)–C(50)	1.490(3)
C(50)–O(50)	1.209(3)
C(50)–O(51)	1.331(3)
O(51)–C(51)	1.442(3)
C(6)–O(1)–C(2)	117.73(16)
O(1)–C(2)–O(3)	109.79(16)
C(2)–O(3)–C(4)	116.77(15)
O(3)–C(4)–C(5)	115.99(17)
C(4)–C(5)–C(6)	119.95(19)
C(5)–C(6)–O(1)	119.61(19)
C(11)–C(2)–C(20)	117.04(17)
O(4)–C(4)–O(3)	117.85(19)
O(4)–C(4)–C(5)	126.11(19)
C(6)–C(5)–C(50)	124.91(19)
C(4)–C(5)–C(50)	115.12(18)
O(1)–C(6)–C(60)	111.68(18)
C(5)–C(6)–C(60)	128.7(2)
C(10)–C(11)–C(12)	121.70(19)
C(10)–C(11)–C(2)	113.50(18)
C(12)–C(11)–C(2)	124.61(17)
O(10)–C(10)–C(11)	177.1(2)
O(12)–C(12)–C(11)	119.13(19)
O(12)–C(12)–C(13)	120.66(19)
C(11)–C(12)–C(13)	120.15(17)
O(50)–C(50)–O(51)	124.3(2)
O(50)–C(50)–C(5)	124.1(2)
O(51)–C(50)–C(5)	111.67(17)
C(50)–O(51)–C(51)	114.99(17)
C(6)–O(1)–C(2)–O(3)	–47.0(2)
O(1)–C(2)–O(3)–C(4)	49.8(2)
C(2)–O(3)–C(4)–C(5)	–25.0(2)
O(3)–C(4)–C(5)–C(6)	–5.2(3)
C(4)–C(5)–C(6)–O(1)	8.3(3)
C(5)–C(6)–O(1)–C(2)	19.1(3)
O(3)–C(2)–C(11)–C(10)	–18.6(2)
O(3)–C(2)–C(11)–C(12)	156.49(18)
C(11)–C(12)–C(13)–C(16)	178.2(2)
O(1)–C(2)–C(20)–C(21)	–178.92(17)
C(4)–C(5)–C(50)–O(51)	63.5(2)
O(50)–C(50)–O(51)–C(51)	6.8(3)

were solved by direct methods (SHELXS-97)¹⁸ and refined by full-matrix least-squares techniques against F^2 (SHELXL-97).¹⁹ The H-atoms of the methyl groups were refined with common isotropic displacement parameters for the H-atoms of the same methyl group and idealized geometry with tetrahedral angles, staggered conformation, and C–H distances of 0.98 Å. The C–H distances of the tertiary hydrogen atoms of the isopropyl groups were constrained to 1.00 Å. See Table 2 for selected bond lengths and angles.

X-Ray structure determination of A. $C_{28}H_{44}N_2O_7$, M_r 520.65, monoclinic, space group $P2_1/n$, $a = 16.964(5)$ Å, $b = 11.267(3)$ Å, $c = 17.010(5)$ Å, $\beta = 117.62(2)^\circ$, $V = 2880.7(14)$ Å³, $Z = 4$, $d_{\text{calc}} = 1.200$ g cm^{–3}, $\mu = 0.086$ mm^{–1}. A total of 6210 reflections were collected ($\theta_{\text{max}} = 25^\circ$), of which 5063 were unique ($R_{\text{int}} = 0.0308$), with 3621 having $I > 2\sigma(I)$. All equivalent bonds in the two parts of the disordered isopropylimino and methoxy groups were restrained to the same length; the *tert*-butyl group dis-

Table 2 Selected bond lengths (Å) and angles (°) for *R,S*-**7b** (A) and *R,R*-**7b** (B)

	<i>R,S</i> - 7b	<i>R,R</i> - 7b
O(1)–C(2)	1.426(3)	1.442(3)
C(2)–O(3)	1.435(3)	1.423(3)
O(3)–C(4)	1.362(3)	1.371(5)
C(4)–C(5)	1.441(3)	1.446(4)
C(5)–C(6)	1.346(3)	1.360(4)
O(1)–C(6)	1.343(3)	1.348(3)
C(4)–O(4)	1.205(3)	1.204(3)
C(2)–C(30)	1.562(3)	1.565(3)
N(10)–C(20)	1.373(3)	1.369(3)
C(20)–C(30)	1.564(3)	1.572(3)
C(30)–C(40)	1.541(3)	1.578(3)
N(10)–C(40)	1.412(3)	1.408(3)
N(10)–C(11)	1.474(3)	1.469(3)
C(20)–O(20)	1.200(3)	1.198(3)
C(30)–C(31)	1.549(3)	1.557(3)
C(31)–O(31)	1.207(3)	1.207(3)
C(40)–N(40)	1.247(3)	1.244(3)
N(40)–C(41)	1.507(5)	1.476(3)
C(6)–O(1)–C(2)	124.01(18)	123.42(19)
O(1)–C(2)–O(3)	113.56(19)	114.5(2)
C(2)–O(3)–C(4)	123.49(19)	121.5(4)
O(3)–C(4)–C(5)	117.7(2)	117.4(3)
C(6)–C(5)–C(4)	120.5(2)	121.6(3)
C(5)–C(6)–O(1)	120.6(2)	118.7(2)
O(1)–C(2)–C(30)	107.01(18)	102.52(19)
O(3)–C(2)–C(30)	103.97(18)	106.0(7)
O(4)–C(4)–O(3)	117.2(2)	116.9(3)
O(4)–C(4)–C(5)	125.0(2)	125.6(3)
O(4)–C(5)–C(51)	113.9(2)	113.3(3)
C(6)–C(5)–C(51)	125.5(2)	125.0(3)
O(1)–C(6)–C(61)	110.1(2)	111.2(2)
C(5)–C(6)–C(61)	129.2(2)	130.0(2)
C(20)–N(10)–C(40)	94.4(2)	95.63(19)
C(20)–N(10)–C(11)	129.1(2)	135.0(2)
C(40)–N(10)–C(11)	136.5(2)	129.1(2)
O(20)–C(20)–N(10)	130.0(2)	132.0(2)
O(20)–C(20)–C(30)	138.2(2)	135.8(2)
N(10)–C(20)–C(30)	91.9(2)	92.19(19)
C(20)–C(30)–C(40)	82.34(18)	81.59(18)
N(40)–C(40)–N(10)	138.0(2)	126.0(2)
N(40)–C(40)–C(30)	130.6(2)	143.4(2)
N(10)–C(40)–C(30)	91.3(2)	90.46(18)
C(40)–N(40)–C(41)	126.4(4)	121.9(2)
C(6)–O(1)–C(2)–O(3)	–2.5(3)	–12.3(9)
O(1)–C(2)–O(3)–C(4)	0.9(3)	19.3(17)
C(2)–O(3)–C(4)–C(5)	2.0(3)	–12.5(18)
O(3)–C(4)–C(5)–C(6)	–3.7(3)	–2.8(12)
C(4)–C(5)–C(6)–O(1)	2.2(4)	9.7(7)
C(5)–C(6)–O(1)–C(2)	1.0(3)	–1.7(4)
C(2)–O(3)–C(4)–O(4)	–178.6(2)	169.9(10)
O(3)–C(4)–C(5)–C(51)	179.8(2)	178.4(9)
C(4)–C(5)–C(51)–O(51)	93.7(3)	–78.2(6)
C(11)–N(10)–C(20)–O(20)	–2.9(5)	–2.9(5)
C(21)–C(2)–C(30)–C(40)	–173.9(2)	174.0(2)
O(1)–C(2)–C(30)–C(31)	–58.5(3)	–178.41(18)
O(3)–C(2)–C(30)–C(31)	–178.94(19)	61.2(5)
O(1)–C(2)–C(30)–C(20)	155.11(18)	–33.9(2)
O(3)–C(2)–C(30)–C(20)	34.7(2)	–154.2(4)
O(20)–C(20)–C(30)–C(40)	–178.0(3)	176.5(3)
N(10)–C(20)–C(30)–C(40)	1.76(18)	–2.61(17)
C(11)–N(10)–C(40)–N(40)	5.5(6)	–0.1(4)
N(10)–C(40)–N(40)–C(41)	–13.2(6)	–176.0(2)

ordered around the C6–C61 bond was refined without any constraints. Equal site occupation factors (SOFs) were given to the disordered methoxy and *tert*-butyl groups [0.525(5) and 0.475(5)]; the SOFs of the isopropylimino group were 0.503(5) and 0.497(5). All the non-hydrogen atoms were refined with anisotropic displacement parameters. For 433 parameters final R indices of $R = 0.0601$ and $wR_2 = 0.1279$ (GOF = 1.084) were obtained. The largest peak in a difference Fourier map was 0.209 e Å^{–3}.

X-Ray structure determination of B. $C_{28}H_{44}N_2O_7$, M_r 520.65, orthorhombic, space group $P2_12_12_1$, $a = 9.885(3)$ Å, $b = 16.338(5)$ Å, $c = 17.537(5)$ Å, $V = 2832.2(15)$ Å³, $Z = 4$, $d_{calc} = 1.221$ g cm⁻³, $\mu = 0.087$ mm⁻¹. A total of 3991 reflections were collected ($\theta_{max} = 25^\circ$), of which 3660 were unique ($R_{int} = 0.0233$), with 3296 having $I > 2\sigma(I)$. All equivalent bonds in the two parts of the disordered group consisting of the methoxy-carbonyl group and the atoms O3, C4, O4 and C5 of the 1,3-dioxin-4-one ring [SOFs of 0.714(4) and 0.286(4)] were restrained to the same length. The non-hydrogen atoms of the less occupied disordered fragment were refined with isotropic displacement parameters; all other non-hydrogen atoms were refined with anisotropic displacement parameters. Due to the absence of heavier atoms the absolute structure cannot be determined reliably: the Flack parameter²⁰ for the inverted absolute structure resulted in 3.4(12) instead of $-2.4(12)$. For 386 parameters final R indices of $R = 0.0400$ and $wR_2 = 0.0915$ ($-GOF = 1.042$) were obtained. The largest peak in a difference Fourier map was 0.169 e Å⁻³.

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