(*R*)-(+)-Pantolactone Acrylate as a Chiral Auxiliary in the Baylis-Hillman Reaction

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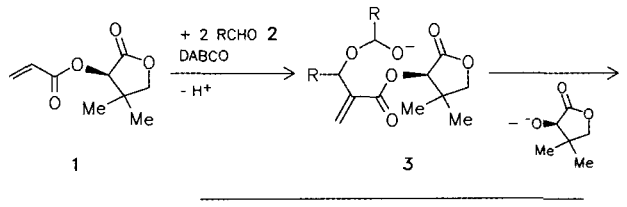
Received January 27, 1993

Key Words: Baylis-Hillman reaction / 1,3-Dioxan-4-ones, 5-methylene- / Trichloroacetaldehyde / Pantolactone

2,6-Dialkyl-5-methylene-1,3-dioxan-4-ones were prepared in good diastereomeric excess by treating pantolactone acrylate with a series of selected aldehydes in the Baylis-Hillman reaction. With benzaldehyde and trichloroacetaldehyde, noncyclic products resulted. In the case of the latter aldehyde the α-hydroxyalkyl acrylate **5b** was isolated as a single diastereomer and its absolute configuration established by X-ray crystallography.

We have earlier reported[1] on the diastereoselective synthesis of 2,6-dialkyl-5-methylene-1,3-dioxan-4-ones by using the versatile Baylis-Hillman reaction[2]. The significant features of our initial findings centered on (i) the accelerating effect which the choice of pantolactone ester exerted on the overall rate of the reaction and (ii) the observation that intramolecular transesterification afforded novel dioxanone derivatives in high chemical yields and in good diastereoisomeric excesses (Scheme 1).

Scheme 1. Formation of 1,3-dioxanone derivatives



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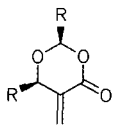

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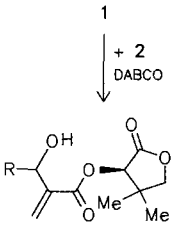
4	R	Yield (%)	d.e. (%)	e.e. at C-2 (%)
a	Me	84	87	10
b	Et	89	78	–
c	*i*Pr	78	81	22
d	Bu	77	78	–
e	c-C_6H_{11}	61	86	39

We have proposed a mechanism for the formation of the dioxanones[1] which involves participation of two molecules of the aldehyde prior to cyclization. It was furthermore established, from NOE studies, that the dioxanone derivatives adopt the *cis* configuration shown in **4a**.

Results and Discussion

In the present work we describe the synthesis of additional 1,3-dioxanone derivatives by employing a range of aliphatic aldehydes as substrates. To our surprise, no cyclization took place when benzaldehyde was employed. Only the "conventional" noncyclic Baylis-Hillman product was isolated (Scheme 2).

Scheme 2. Formation of noncyclic products



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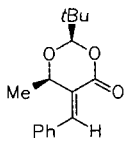
5	R	Yield (%)	d.e. (%)	e.e. at C-2 (%)
a	Ph	81	2	–
b	CCl_3	83	48	–

1,3-Dioxan-4-ones

Prior to the recent work by Seebach et al.[3] on the synthesis and use of 1,3-dioxan-4-ones, little had been reported in the literature in this field. In much earlier studies Hennes and Gundinger[4] refer to the formation of chlorinated derivatives from chloral hydrate and a chlorinated 3-hydroxy acid. Kahn and Cohen[5] also report on the effect of 2,2,6-trimethyl-1,3-dioxan-4-one cation transfer in human erythrocytes. In the early 1970s, Ayras and Pihlaja[6] described the synthesis of 1,3-dioxan-4-ones from 3-hydroxy acids and appropriate aldehydes. The full synthetic potential of these



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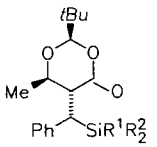

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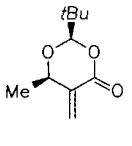

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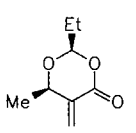

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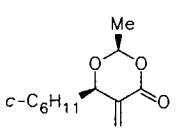

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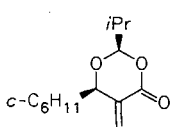

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compounds was finally exposed in a series of papers by Seebach et al.[7]. Only some selected examples from this work will be highlighted here[8]. Thus, the benzylidene derivative **6**, which bears the closest resemblance to our 5-methylene-1,3-dioxan-4-one derivatives, undergoes Michael addition with silyl reagents to afford the single stereoisomer **7**.

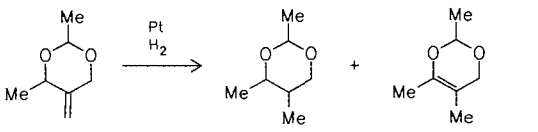
Seebach et al.[9] did in fact prepare the dioxanone **8** bearing an exocyclic methylene group as is found in our derivatives, but this was achieved by selenylation followed by oxidative elimination. It is necessary to emphasize that the dioxanones obtained by the Seebach procedure invariably involve the reaction of (*R*)- or (*S*)-3-hydroxybutanoic acid with an aldehyde whereas in our protocol the pantolactone ester is the crucial component. Through careful control of temperature and by limiting the excess of aldehyde, it has been possible to obtain the variously substituted dioxanones **9**–**11**.

Stereochemistry of the 1,3-Dioxan-4-ones

The degree of diastereoselectivity achieved by our method of synthesis is good (78–87%). However, the enantioselectivity was disappointingly low with values considerably lower than those obtained by Seebach et al. If the *cis* configuration shown in **4** is assumed for all our compounds, it can be deduced that the observed d.e. arises from the excess of the (*RR*)/(*SS*) enantiomeric pair over the (*RS*)/(*SR*) pair. This excess was readily established by examination of the ^{1}H-NMR spectra at 200 MHz.

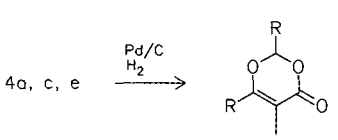
In order to establish the enantiomeric excess at the second center formed, i.e. at C-2, we made use of a fortuitous discovery which we subsequently found had previously been exploited by other researchers. Thus, Anteunis and Camerlynck[10] had hydrogenated (Pt/H_2) compound **12** and obtained a mixture of **13** and **14** (Scheme 3). In even earlier reports, Hubert and Reimlinger[11] reported the isomerization of exocyclic olefins to the endocyclic isomers. Similar effects are described by Seebach et al. in the recent literature[12].

Scheme 3. Partial isomerization of exocyclic double bonds



We have established the generality of the isomerization by treating our dioxanones with Pd/H_2, and in each case the dioxine derivative was the sole product. This is illustrated for **4a**, **c** and **e** in Scheme 4. If the contributions of the minor diastereomers (*RS*)/(*SR*) are ignored then use of a chiral shift reagent should allow determination of the enantiomeric excess at C-2 in the dioxin. The values obtained in this way are low, but there is a steady increase in enantioselctivity as the steric bulk of aldehyde increases from acetaldehyde to isobutyraldehyde to cyclohexanecarboxaldehyde.

Scheme 4. Complete isomerization of exocyclic double bond



15	R
a	Me
b	*i*Pr
c	*c*-C_6H_{11}

Acyclic Products

When benzaldehyde failed to give a cyclic product on reaction with the pantolactone ester under the usual conditions, steric hindrance was thought to prevent cyclization. However, when bulky aldehydes such as isobutyraldehyde and cyclohexanecarboxaldehyde cyclized smoothly and with a high degree of diastereoselectivity this postulate had to be revised. The findings are possibly better explained on electronic grounds in which the nucleophilicity of the oxy anion intermediate (Scheme 1) influences the course of the reaction. According to March[13] the order of nucleophilicity for a selected series of anions is:

$$H_2N^- > RO^- > HO^- > R_2\ddot{N}H > ArO^-$$

The phenoxide anion is therefore regarded as a weak nucleophile. Our finding that trichloroacetaldehyde also does not cyclize can be rationalized on a similar basis. Although the three chloro atoms make this aldehyde a very strong electrophile, their strong effect reduces the nucleophilicity of the resultant oxy anion and inhibits the subsequent cyclization step.

The properties of **5b**, the product from the trichloroacetaldehyde reaction, on account of its very rapid formation and its crystalline nature, were studied in detail. Attempts to separate the major diastereomer from the 74:26 mixture by recrystallization proved to be unsuccessful. However, when chloroform was employed as solvent, recrystallization furnished exclusively the minor diastereomer ($[\alpha]_D^{27} = -8.6$). From its X-ray data it could be established that the absolute configuration at the newly created center at C-3 was (*S*), and this implies that the major isomer has the (*R*) configuration (Figure 1).

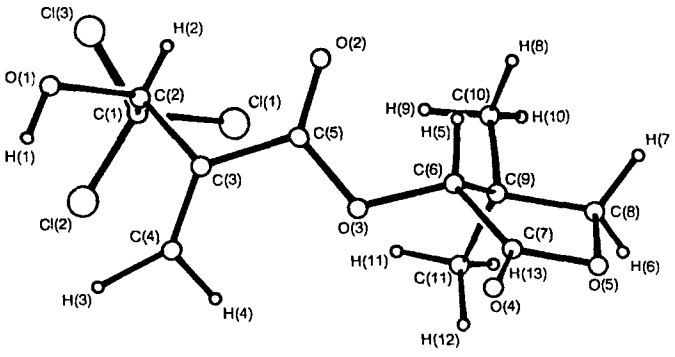
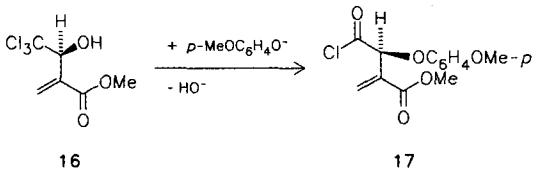


Figure 1. Molecular structure of **5b** in the crystal

By further extrapolation it can be concluded that (i) the configuration of the predominant stereoisomer in the 1,3-dioxan-4-one series of compounds is (*S*) at C-3 (change of priority of substituents) and (ii) the enantiomeric excess observed are due to an excess of the (*S,S*) enantiomer over the (*R,R*) enantiomer.

The crystalline, and optically pure minor diastereomer of **5b** possesses further interesting features. It can be converted by simple hydrolysis into the enantiomerically pure acid **16**. According to a very recent publication[14], this type of compound is readily converted into the versatile synthetic intermediate **17** (Scheme 5). Work on this reaction is in progress.

Scheme 5. Conversion of **16** into the synthetic intermediate **17**



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This work has been supported by the *Foundation for Research Development* (FRD) and by the *Natal University Research Fund.*

Experimental

^{1}H and ^{13}C NMR: Varian Gemini 200 (200 MHz); TMS/$CDCl_3$ as internal standards unless otherwise specified. – NOE: Bruker WM 500 (500 MHz) and Gemini 200 (200 MHz). – Elemental analyses: Perkin-Elmer 2400 Elemental Analyzer. – High-resolution MS: Varian MAT 212 Mass Spectrometer. – GC/MS: Hewlett-Packard 5890 Gas Chromatograph and 5988A Spectrometer. – Specific rotations: Perkin-Elmer 241 Polarimeter.

The general method of synthesis and the spectral properties of **4a**, **9** and 6-ethyl-2-methyl-5-methylene-1,3-dioxan-4-one have been described in our preliminary communication[1].

2,6-Diethyl-5-methylene-1,3-dioxan-4-one (**4b**): A mixture of pantolactone acrylate [0.50 g (2.72 mmol)], propionaldehyde [0.40 g (6.80 mmol)] and DABCO [0.10 g (20 mol-% of the ester)] was stirred in a sealed vessel at 24°C until the reaction was complete (usually 30 min). Column chromatography (SiO_2; ethyl acetate/hexane) afforded pure **4b** [0.33 g (89%)], $[\alpha]_D^{26} = -5.34$ ($c = 1.03$ in $CHCl_3$). – ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.02$ (t, $J = 7.4$ Hz, 6H, 2 CH_3), 1.62–1.99 (m, 4H, 2 CH_2), 4.54 (m, 1H, 6-H), 5.28 (t, $J = 5.0$ Hz, 1H, 2-H), 5.61 and 6.49 (2 dd, $J = 0.4$ Hz, 2H,H_2). – ^{13}C NMR: $\delta = 7.39$ (q, 6-CH_3), 8.89 (q, 2-CH_3), 27.64 (t, 6-CH_2), 28.02 (t, 2-CH_2), 78.50 (d, C-6), 102.68 (d, C-2), 125.41 (t,H_2), 136.87 (s, C-5), 164.19 (s, C=O). – MS (70 eV): *m/z* (%) = 170 (1) [M^+], 141 (48), 95 (25), 83 (100), 67 (73), 68 (44) and 43 (40). – $C_9H_{14}O_3$: calcd. 170.09428; found 170.09360 (MS).

2,6-Diisopropyl-5-methylene-1,3-dioxan-4-one (**4c**): Prepared as above from 0.49 g (6.80 mmol) of isobutyraldehyde; yield 0.42 g (78%), $[\alpha]_D^{25} = -18.74$ ($c = 1.03$ in $CHCl_3$). – ^{1}H NMR: $\delta = 0.9$, 1.01, 1.02 and 1.05 (d, $J = 7.0$ Hz, 12H, 4 CH_3), 1.93–2.18 [m, 2H, $CH(CH_3)_2$], 4.48 (m, 1H, 6-H), 5.03 (d, $J = 4.5$ Hz, 1H, 2-H), 5.56 and 6.44 (dd, $J = 0.48$ Hz, 2H,H_2). – ^{13}C NMR: $\delta = 15.47$ and 16.01 [q, 6-$CH(CH_3)_2$], 16.81 and 18.61 [q, 2-$CH(CH_3)_2$], 32.26 (d, 6-CH), 33.59 (d, 2-CH), 81.54 (d, C-6), 104.07 (d, C-2), 125.31 (t, $=CH_2$), 136.63 (s, C-5), 165.46 (s, C=O). – MS (70 eV): *m/z* (%) = 198 (1) [M^+], 156 (26), 125 (33), 109 (29), 84 (29), 83 (100), 67 (38), 56 (22). – $C_{11}H_8O_3$: calcd. 198.12558; found 198.12330 (MS).

2,6-Dibutyl-5-methylene-1,3-dioxan-4-one (**4d**): Prepared as above from 0.59 g (6.80 mmol) of valeraldehyde; yield 0.47 g (77%), $[\alpha]_D^{22} = -12.67$ ($c = 0.87$ in $CHCl_3$). – ^{1}H NMR: $\delta = 0.92$ (t, $J = 7.0$ Hz, 6H, 2 CH_3), 1.30–1.51 [m, 8H, 2 $(CH_2)_2$], 1.68–1.86 (m, 4H, 2-, 6-CH_2), 4.55 (m, 1H, 6-H), 5.31 (t, $J = 5.2$ Hz, 1H, 2-H), 5.60 and 6.46 (d, 2H,H_2). – ^{13}C NMR: $\delta = 13.92$ and 13.97 (q, CH_3), 22.41, 22.57, 25.30 and 26.80 [t, 2 $(CH_2)_2$], 34.21 (t, 6-CH_2), 34.81 (t, 2-CH_2), 77.86 (d, C-6), 102.38 (d, C-2), 125.61 (t,H_2), 137.26 (s, C-5), 164.12 (s, C=O). – MS (70 eV): *m/z* (%) = 226 (0.1) [M^+], 169 (59), 123 (24), 95 (39), 83 (100), 81 (26), 55 (17). – $C_{13}H_{22}O_3$ (226): calcd. C 68.99, H 9.80; found C 68.91, H 9.81.

2,6-Dicyclohexyl-5-methylene-1,3-dioxan-4-one (**4e**): Prepared as above from 0.76 g (6.80 mmol) of cyclohexanecarboxaldehyde; yield 0.46 g (61%), $[\alpha]_D^{21} = -27.37$ ($c = 1.08$ in $CHCl_3$). – ^{1}H NMR: $\delta = 1.09-1.83$ (m, 22H, cyclohexyl), 4.42 (m, 1H, 6-H), 4.98 (d, $J = 4.7$ Hz, 2H, 2-H), 5.53 and 6.39 (dd, 2H,H_2). – ^{13}C NMR: $\delta = 25.62$, 25.63, 25.98, 26.18, 26.29, 26.31, 26.41, 26.42, 26.63 and 29.08 (t, CH_2, cyclohexyl), 41.75 (d, 6-CH, cyclohexyl), 43.69 (d, 2-CH, cyclohexyl), 81.72 (d, C-6), 103.9 (d, C-2), 125.40 (t,H_2), 136.65 (s, C-5), 165.69 (s, C=O). – MS (70 eV): *m/z* (%) = 196 (36), 195 (35), 149 (30), 96 (100), 95 (36), 83 (69), 81 (58), 55 (71). – $C_{17}H_{26}O_3$ (278): calcd. C 73.35, H 9.41; found C 73.29, H 9.34.

4,4-Dimethyl-2-oxotetrahydrofuran-3-yl 3-Hydroxy-2-methylene-3-phenylpropanoate (**5a**): Prepared as before from 0.72 g (6.80 mmol) benzaldehyde; yield 0.64 g (81%) of white crystals, m.p. 49–52°C, $[\alpha]_D^{28} = +8.2$ ($c = 0.92$ in $CHCl_3$). – ^{1}H NMR: $\delta = 0.90$ and 1.09 (s, 6H, 2 CH_3), 2.90 (br. d, 1H, OH), 3.99 (s, CH_2O), 5.34 (s, 1H, CH, ring), 5.62 (br. d, 1H, CHOH), 6.02 and 6.49 (m, 2H,H_2), and 7.27–7.41 (m, 5H, aromatic). – ^{13}C NMR: $\delta = 19.64$ and 22.91 (q, 2 CH_3), 40.38 [s, $C(CH_3)_2$], 72.65 (d, ring CHO), 72.49 (d, CHOH), 76.21 (t, CH_2, ring), 126.36, 126.96 and 128.49 (d, CH, aroamtic), 128.09 (t,H_2), 140.8 (s, C, aromatic), 141.03 (s, C=CH_2), 164.74 (s, C=O, ring), 172.21 (s, C=O). – MS (70 eV): *m/z* (%) = 290 (13) [M^+], 177 (43), 169 (28), 160 (82), 159 (52), 132 (100), 115 (40), 105 (65), 99 (64). – $C_{16}H_{18}O_5$ (290): calcd. 290.1154; found 290.1182 (MS).

4,4-Dimethyl-2-oxotetrahydrofuran-3-yl 4,4,4-Trichloro-3-hydroxy-2-methylenbutanoate (**5b**): Prepared as before from 1.00 g (6.80 mmol) of trichloroacetaldehyde; yield 0.75 g (83%) of white needles, m.p. 118–120°C, as a mixture of diastereomers. Recrystallization from $CHCl_3$ gave the pure *minor* diastereomer, m.p. 165°C, $[\alpha]_D^{27} = -8.6$ ($c = 1.1$ in $CHCl_3$). – ^{1}H NMR: $\delta = 1.18$ and 1.24 (s, 6H, 2 CH_3), 3.94 (d, 1H, OH), 4.09 (dd, $J = 1.3$ Hz, 2H, CH_2, ring), 4.53 (br. d, 1H, OH), 5.34 (br. d, 1H, CHOH), 5.48 (s, 1H, CH, ring), 6.44 and 6.79 (d, $J = 0.4$ Hz, 2H,H_2). – ^{13}C NMR: $\delta = 20.01$ and 23.03 (q, 2 CH_3), 40.54 [s, $C(CH_3)_2$], 75.87 (d, CH, ring), 76.18 (t, CH_2, ring), 79.95 (d, CHOH), 101.95 (s, CCl_3), 133.82 (t,H_2), 134.58 (s, C=CH_2), 165.23 (s, C=O, ring), 171.81 (s, C=O). – MS (70 eV): *m/z* (%) = 303 (15), 213 (62), 165 (94), 113 (100), 83 (62). – $C_{11}H_{13}Cl_3O_5$ (331): calcd. C 39.85, H 3.95; found C 39.69, H 3.92.

6-Cyclohexyl-2-methyl-5-methylene-1,3-dioxan-4-one (**10**): The general procedure has been described[1]. In this instance cyclohexanecarboxaldehyde [0.41 g (3.66 mmol)] was added first, followed by acetaldehyde [0.16 g (3.70 mmol)]. The product [0.40 g (52%)] was an oil $[\alpha]_D^{26} = -10.9$ ($c = 1.05$ in $CHCl_3$). – ^{1}H NMR: $\delta = 1.09$ and 1.84 (m, 11H, cyclohexyl), 1.51 (d, $J = 5.15$ Hz, 3H, CH_3), 4.49 (m, 1H, 6-H), 5.40 (q, $J = 5.13$ Hz, 1H, 2-H), 5.56 and 6.40 (dd, $J = 0.5$ Hz, 2H, $=CH_2$). – ^{13}C NMR: $\delta = 20.42$ (q, CH_3),

25.93–28.84 (t, CH_2, cyclohexyl), 43.54 (t, CH, cyclohexyl), 81.61 (d, J = Hz, C-6), 98.26 (d, C-2), 125.34 (t, $=CH_2$), 136.23 (s, $C=CH_2$), 165.41 (C=O). – MS (70 eV): m/z (%) = 209 (0.2), 128 (88), 84 (100), 83 (32), 55 (17). – $C_{12}H_{12}O_3$ (212): calcd. C 68.55, H 8.63; found C 68.78, H 8.68.

6-Cyclohexyl-2-isopropyl-5-methylene-1,3-dioxan-4-one (**11**): Reaction with cyclohexanecarboxaladehyde [0.41 g (3.66 mmol)] followed by isobutyraldehyde [0.27 g (3.70 mmol)] gave an oil [0.44 g (50%)]; $[\alpha]_D^{24} = -16.1$ (c = 1.02 in $CHCl_3$). – ^{1}H NMR: δ = 0.99 and 1.03 (d, J = 1.74 Hz, 6H, 2 CH_3), 0.98–2.09 (m, 11H, cyclohexyl), 4.45 (m, 1H, 6-H), 4.99 (d, J = 4.5 Hz, 1H, 2-H), 5.54 and 6.40 (m, 2H, $=CH_2$). – ^{13}C NMR: δ = 16.11 and 16.26 (q, 2 CH_3), 25.55–29.09 (t, CH_2, cyclohexyl), 32.23 [d, $CH(CH_3)_2$], 41.63 (d, CH, cyclohexyl), 81.66 (d, C-6), 104.33 (d, C-2), 125.46 (t,H_2), 136.63 (s, $C=CH_2$), 165.68 (s, C=O). – MS (70 eV): m/z (%) = 237 (0.2), 156 (100), 95 (13), 84 (77), 55 (14). – $C_{14}H_{22}O_3$ (238): calcd. C 70.56, H 9.30; found C 70.30, H 9.46.

2,5,6-Trimethyl-2H,4H-1,3-dioxin-4-one (**15a**): The dioxanone **4a** [1.00 g (7.04 mmol)] in methanol (10 ml) was treated with a catalytic amount of Pd/C (10%). Hydrogenation proceeded until all the starting material had disappeared. The pure product was obtained after column chromatography as an oil [0.85 g (85%)], $[\alpha]_D^{24} = +30.7$ (c = 1.1 in $CHCl_3$). – ^{1}H NMR: δ = 1.62 (d, J = 5.33 Hz, 3H, 2-CH_3), 1.83 and 2.04 (s, 6H, 5-, 6-CH_3), 5.54 (q, J = 5.2 Hz, 1H, 2-H). – ^{13}C NMR: δ = 10.59 (q, 5-CH_3), 16.99 (q, 6-CH_3), 19.55 (q, 2-CH_3), 97.48 (d, C-2), 102.77 (s, C-5), 164.74 (s, C-6), 166.83 (s, C=O). – MS (70 eV): m/z (%) = 142 (32) [M^+], 98 (76), 83 (65), 70 (86), 56 (41), 43 (100). – $C_7H_{10}O_3$ (142): calcd. C 59.15, H 7.09; found C 59.20, H 7.12.

2,6-Diisopropyl-5-methyl-2H,4H-1,3-dioxin-4-one (**15b**): This was obtained in 86% yield from **4c** by the standard procedure described for **15a**; $[\alpha]_D^{24} = +48.3$ (c = 0.9 in $CHCl_3$). – ^{1}H NMR: δ = 1.05–1.16 (d, J = 6.8 Hz, 12H, 4 CH_3), 1.84 (s, 3H, 5-CH_3), 2.15 [m, 1H, 6-$CH(CH_3)_2$], 2.89 [m, 1H, 2-$CH(CH_3)_2$], 5.05 (d, J = 4.7 Hz, 1H, 2-H). – ^{13}C NMR: δ = 9.93 (q, 5-CH_3), 15.98, 16.26, 18.54 and 19.55 [q, $CH(CH_3)_2$], 29.38 [d, 6-$CH(CH_3)_2$], 31.44 [d, 2-$CH(CH_3)_2$], 100.44 (s, C-5), 103.14 (s, C-2), 165.19 (s, C-6), 173.01 (s, C=O). – MS (70 eV): m/z (%) = 198 (4) [M^+], 127 (22), 126 (30), 98 (11), 83 (100), 7 (13), 43 (7). – $C_{11}H_{18}O_3$ (198): calcd. C 66.64, H 9.15; found C 66.84, H 9.39.

2,6-Dicyclohexyl-5-methyl-2H,4H-1,3-dioxin-4-one (**15c**): This was isolated in 97% yield from **4e** by the procedure used for **15a**; m.p. 54–55°C, $[\alpha]_D^{25} = +45.5$ (c = 0.7 in $CHCl_3$). – ^{1}H NMR: δ = 1.05–1.91 (m, 21H, cyclohexyl), 1.83 (s, 3H, 5-CH_3), 2.53 (m, 1H, 6-CH, cyclohexyl), 5.05 (d, J = 4.5 Hz, 1H, 2-H). – ^{13}C NMR: δ = 9.98 (q, 5-CH_3), 25.45–29.45 (t, CH_2, cyclohexyl), 39.52 (d, 6-CH, cyclohexyl), 40.70 (d, 2-CH, cyclohexyl), 100.62 (s, C-5), 102.50 (d, C-2), 165.18 (s, C-6), 172.56 (s, C=O). – MS (70 eV): m/z (%) = 278 (6) [M^+], 167 (97), 137 (26), 111 (36), 98 (69), 83 (100), 55 (18). – $C_{17}H_{26}O_3$ (278): calcd. C 73.35, H 9.41; found C 73.07, H 9.59.

X-ray Crystal-Structure Analysis of **5b**[15]: Large, white crystals from $CHCl_3$. – Crystal data: $C_{11}H_{13}Cl_3O_5$ (331.57); crystal size 2.3 × 0.31 × 0.23 mm; orthorhombic; space group $P2_12_12_1$; a = 6.199(3), b = 10.173(1), c = 22.976(3) Å; Z = 4; $d_{calcd.}$ = 1.540 g cm^{-3}. – Data collection: Enraf-Nonius CAD-4 four-circle diffractometer; graphite-monochromated Mo-K_α radiation (λ = 71.069 pm, ω/2Θ-scan technique); 2154 independent measured reflections, 1738 observed with $I > 3\sigma(I)$; empirical absorption correction [μ(Mo-K_α) = 352.13 cm^{-1}]. – Structure solution and refinement: Direct methods and refinement by full-matrix least-squares technique[16] (200 parameters). Atomic scattering factors and anomalous dispersion corrections were taken from International Tables for X-ray Crystallography[17]. R = 0.0574 {R_w = 0.0622; $w = 1.0/[\sigma^2(F) + 0.000707\ F^2]$}. Residual electron density Δϱ = 26.9 e/nm^3. Positional and thermal parameters of nonhydrogen atoms are given in Table 1.

Table 1. Fractional coordinates (× 10^{-4}) for the nonhydrogen atoms of **5b**

	x/a	y/b	z/c
Cl(1)	5499(3)	6779(1)	2021(1)
Cl(2)	6218(3)	9506(1)	1763(1)
Cl(3)	1852(3)	8498(2)	1812(1)
O(1)	3797(6)	8861(4)	632(2)
O(2)	5351(6)	5112(4)	685(2)
O(3)	8974(5)	5347(3)	705(1)
O(4)	11539(7)	4145(3)	-188(1)
O(5)	12079(7)	2556(3)	453(2)
C(1)	4581(8)	8127(5)	1605(2)
C(2)	4602(9)	7793(4)	951(2)
C(3)	6813(7)	7260(4)	756(2)
C(4)	8469(9)	7995(4)	593(2)
C(5)	6922(8)	5801(4)	711(2)
C(6)	9217(8)	3947(4)	670(2)
C(7)	11042(9)	3630(4)	259(2)
C(8)	11021(12)	2083(5)	982(2)
C(9)	9809(9)	3257(4)	1236(2)
C(10)	7798(11)	2824(6)	1584(2)

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