121. Diastereoface Selectivity During Phthalimidonitrene Additions to (*E*)- and (*Z*)-Configurated α,β-Unsaturated Esters, Induced by a Chiral Center in the γ-Position

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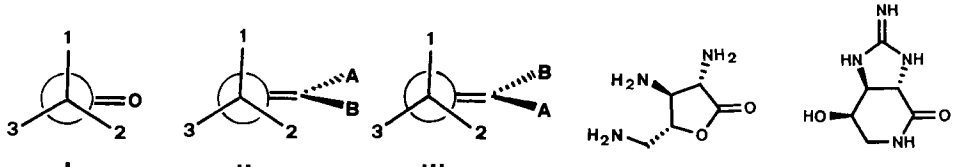
In-situ-generated phthalimidonitrene was added to five α,β-unsaturated esters containing a chiral secondary O-function at C(γ). The additions were fully suprafacial, inasmuch as the (*E*)-isomers **1** afforded only the *trans*-aziridines **2** and **3** ($J(\beta,\gamma)$ = 4.8–5.1 Hz) and the (*Z*)-isomers **4** only the *cis*-aziridines **5** and **6** (8.2–8.5 Hz). The products **2**, **3**, **5**, and **6** where shown to possess the *arabino-*, *xylo-*, *ribo-*, and *lyxo*-configuration, respectively, by X-ray structure analysis of **2b**, **2d**, and **6a**. The diastereoface selectivity of the nitrene additions, induced by the chiral substructure around C(γ), resulted in more **2** than **3** from **1**, but more **6** than **5** from **4**, which means that the preference of attack at the double bond switches from one side to the other depending on the C=C configuration. The preferences were higher at lower temperature. The aziridines **2a**, **2d**, and **3d** exhibit ^{1}H-NMR-visible isomerism at the ring N-atom; the major (78–95%) invertomer **A** is always the one with the phthalimido group in *trans*-position to the (larger) substructure around C(γ). The other aziridines only show ^{1}H-NMR signals of one invertomer, which – by steric reasoning – ought to be **A**; this is confirmed by a ^{1}H-NMR argument for **3a**, **5a**, **6a**, **5c**, and **6c**.

1. Introduction. – With the aim of developing model concepts for asymmetric induction [1], much work has been done concerning the preferred side (diastereoface selectivity) from which a C=O bond in an acyclic system (see **I**) is attacked under the influence of an adjacent chiral center [2]. Less information is available concerning the diastereoface selectivity of attacks on a C=O bond in an acyclic system (see **II** or **III**) under the influence of such a chiral center [3]. An interesting aspect of the latter situation is the effect on the selectivity by the configuration of the double bond [4] [5]. The two situations are more comparable when the C=C bond is conjugated to a C=O group (A = C=O in **II** and **III**), *i.e.* when the chiral center is in vinylogous position to the carbonyl C-atom [5] [6]. The chiral center most frequently present in such cases is a C-atom with a secondary O-function [4–8]. We describe here some other examples of this type, namely nitrene additions to α,β-unsaturated esters containing secondary ether functions at C(γ). We met this problem during exploratory efforts to obtain *arabino*-L-pentonic-acid derivative **IV** (*cf.* [9] [10]) as an intermediate for a synthesis of streptolidine **V**, which is an essential component of the streptothrycin antibiotics [11].



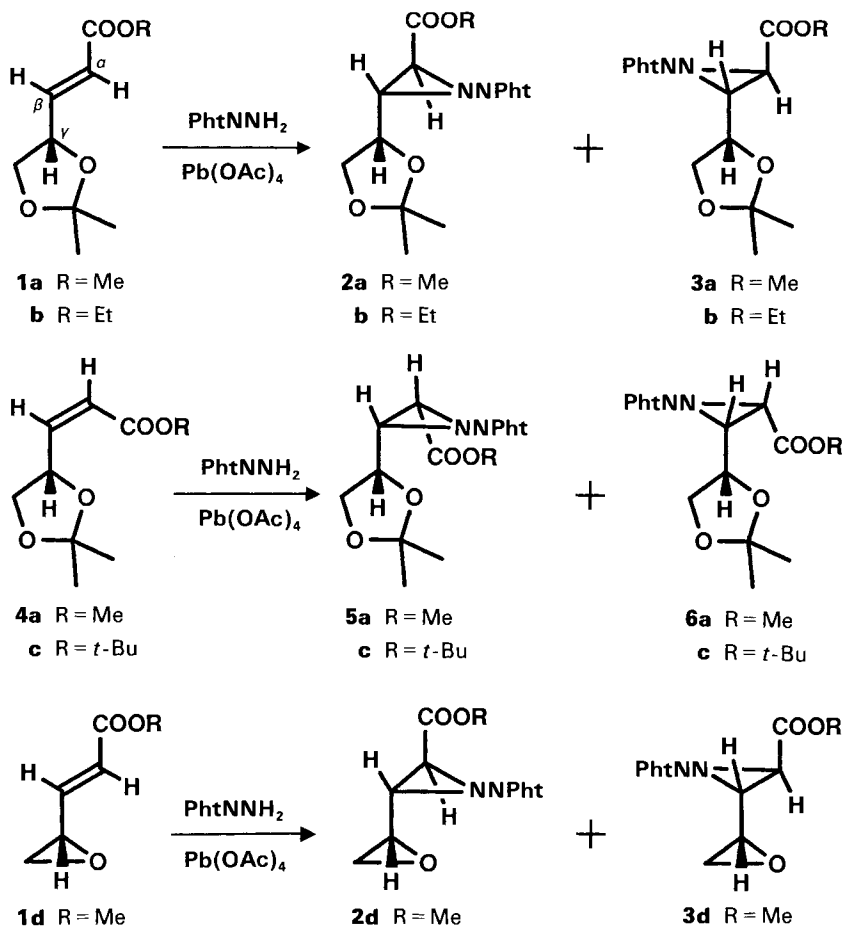
I **II** **III** **IV** **V**

[1]) On leave of absence from Pharmaceutical Institute, Warszawa-Poland.

[2]) Partially from the diploma thesis of *C. B.*, University of Zürich, 1986.

2. Nitrene Additions. – In eight experiments, run in CH_2Cl_2, phthalimidonitrene (PhtNN), generated *in situ* from *N*-aminophthalimide ($PhtNNH_2$) with $Pb(OAc)_4$ [12] [13], was added to the double bond of five α,β-unsaturated esters **1a, b, d** ((*E*)-configuration) and **4a, c** ((*Z*)-configuration), all carrying an H- and O-atom, as well as a CH_2O group at the chirality center C(γ). In all cases, *N*-phthalimidoaziridines were formed, namely **2a, b, d, 3a, b, d, 5a, c**, and **6a, c**, in 72–97% yield for the (*E*)- and 47–64% yield for the (*Z*)-series (see *Schemes* and *Table 1*). Evidence for their configurations are given in *Chapt. 3*. When 1.1 mol-equiv. each of $PhtNNH_2$ and $Pb(OAc)_4$ were used, the nitrene addition was incomplete[3]), but usually most of the unreacted unsaturated ester was recovered. The (*E*)-isomers **1** led only to the *arabino*- and *xylo*-products **2** and **3**,

Scheme



Pht = phthalimido

[3]) This is probably due to the competing side reaction of PhtNN with $PhtNNH_2$ [13]. With 2.2 mol-equiv. each of $PhtNNH_2$ and $Pb(OAc)_4$, the isolated yield of **1a**/**2a** was 79% [14].

Table 1. *Reactions of α,β-Unsaturated Esters* **1** *and* **4** *with Phtalimidonitrene*

Starting material (*E*)	Temp. [°C][a]	**1** (recovered) [%]	**2** (*arabino*)[b] [%]	**3** (*xylo*)[c] [%]	Ratio **2**/**3**
1a (*S*)	0	39	45	14	3.1:1
1a (*S*)	–40	31	57	2	30:1
1b (*RS*)[d]	0	39	46[e]	14	3.3:1
1b (*RS*)[d]	–38	38	58	0.2[f]	290:1
1d (*RS*)[d]	0	25	36[e]	18	2:1
Starting material (*Z*)	Temp. [°C][a]	**4** (recovered) [%]	**5** (*ribo*)[g] [%]	**6** (*lyxo*)[h] [%]	Ratio **5**/**6**
4a (*S*)	0	67	9	12	1:1.3
4a (*S*)	–40	81	4	8	1:2
4c (*S*)	0	53	11	11	1:1

[a]) Temperature of the nitrene generation and addition.
[b]) Result of (*αsi,βsi*)-attack (major).
[c]) Result of (*αre,βre*)-attack.
[d]) For comparison, these racemic samples are represented as (*γS*)-enantiomers.
[e]) Structures of **2b**, **2d**, and **6a** from an X-ray analysis.
[f]) Detected in the mother liquor material after crystallization of **2**.
[g]) Result of (*αre,βsi*)-attack.
[h]) Result of (*αsi,βre*)-attack.

respectively, and the (*Z*)-isomers **4** furnished only the *ribo*- and *lyxo*-products **5** and **6**, respectively.

Thus, all the nitrene additions were – as expected [15] – fully stereoselective at C(α) relative to C(β), namely suprafacial. The diastereoface selectivity (in the following short: selectivity) at C(β) relative to C(γ), which is the subject of this paper, favored the *arabino*-((*αsi,βsi*)-attack) over the *xylo*-products ((*αre,βre*)-attack) in the (*E*)-series **1** by a factor from > 2:1 at 0° up to *ca.* 300:1 at –40° (see **2**/**3**, *Table 1*). In the (*Z*)-series **4**, there was a smaller selectivity, which preferred the *lyxo*- ((*αsi,βre*)-attack) over the *ribo*-isomers ((*αre,βsi*)-attack) by < 1.2:1 at 0° and by 2:1 at –40° (see **5**/**6**, *Table 1*).

Our optically active starting materials **1a**, **4a**, and **4c** as well as the derived products have the (*γS*)-configuration. For the sake of visual comparison, we represent the racemic compounds **1b** and **1d** also by the (*γS*)-enantiomers; the same is true for the products obtained from them[5]).

In the experiments with **1a,b** ((*E*)-configuration) and **4a,c** ((*Z*)-configuration), the chiral induction is due to the 1,3-dioxolan-4-yl unit; the structures (aside from the configurations) of the starting materials differ only in the ester group (Me *vs.* Et *vs.* *t*-Bu). In the (*E*)-series **1**, the (*γS*)-configuration causes the nitrene to attack the (*αsi,βsi*)-side of the C=C bond in preference over the (*αre,βre*)-side by a factor of *ca.* 3:1 at 0° and *ca.* 300:1 at –40°. In the (*Z*)-series **4**, the same unit causes the (*αsi,βre*)-attack to exceed the (*αre,βsi*)-attack *ca.* twofold at –40°. We note that the preferred attack at C(β), the prochiral center adjacent to the inducing chiral substructure around C(γ), switches to the

[4]) Care was taken to avoid purification procedures which might discriminate between the diastereoisomers.
[5]) Our experiments were not designed to critically evaluate an enantiomeric excess effect (EE-effect) [16] involving the racemic samples (**1b**, **1d**) as compared to the enantiomerically pure ones (**1a**, **4a**, **4c**), *cf. Chapt. 6.*

other side when the configuration of the C=C bond is changed. In the starting material **1d**, the inducing chiral substructure around C(γ) is the oxiran-2-yl unit. The selectivity is nevertheless in the same direction, inasmuch as the (γS)-configuration also induces the nitrene to attack the ($\alpha si, \beta si$)-side of this (*E*)-configurated C=C bond in preference over the ($\alpha re, \beta re$)-side, in this case by a factor of *ca.* 2:1 at 0°.

3. Configurations. – 3.1. *Starting Materials.* Most of the α,β-unsaturated esters **1** and **2** have been prepared and configurationally assigned previously in racemic or optically active form, or as another ester (see *Exper. Part,* for hitherto unknown samples). The configurations at the C=C bond follow from the ^{1}H-NMR spectra ($J(\alpha,\beta)$ = 15–16 Hz, for (*E*)-isomers **1** and $J(\alpha,\beta)$ = 10–11 Hz for (*Z*)-isomers **4**[6])) and the absolute configurations of the (*S*)-enantiomers **1a**, **4a**, and **4c** from their preparation from (*R*)-2,3-*O*-isopropylideneglyceraldehyde. The enantiomeric excesses (ee values) of **1a** and **4a** were determined to be > 98% by capillary GC using an optically active stationary phase (calibrated in the case of **1a**). Since **4c** was made by the same reaction from the same starting material as **1a** and **4a**, its ee value was also taken to be > 98%. The racemic samples **1b** and **1d** stemmed from *rac*-2,3-*O*-isopropylideneglyceraldehyde and from (achiral) methyl (2*E*)-penta-2,4-dienoate, respectively.

3.2. *Products.* The spectral properties of the nitrene-addition products of this work, the aziridines **2**, **3**, **5**, and **6**, are highly characteristic; all the relevant signals in the ^{1}H-NMR spectra can be identified unequivocally (see *Table 2*). They show the α,β-*trans*-configuration at the aziridine ring in the *arabino*- and the *xylo*-isomers **2** and **3** ($J(\alpha,\beta)$ = 4.5–5.0 Hz) as well as the α,β-*cis*-configuration in the *ribo*- and the *lyxo*-isomers **5** and **6** ($J(\alpha,\beta)$ = 8.0–8.3 Hz); *cf.* [17]. This, together with the known configuration at the C=C bond in the starting materials, independantly confirms the suprafaciality of the nitrene additions.

Concerning the β,γ-configurations of our products (the feature of major interest of this paper) our arguments are based on the *arabino*-configuration of **2b** and **2d** and on the *lyxo*-configuration of **6a**, all of which were established by X-ray structure analysis (see *Chapt. 5*). This, together with the above conclusions on the α,β-configurations, also fixes the *xylo*-configuration of **3b** and **3d** as well as the *ribo*-configuration of **5a**. We then note that each of our other aziridines shows a remarkable ^{1}H-NMR similarity with one of the already assigned samples, namely **2a** with **2b**, **3a** with **3b**, **5c** with **5a**, and **6c** with **6a** (see *Table 2*). Thus, there can be no doubt about the *arabino-*, *xylo-* *ribo-*, and *lyxo*-configuration of **2a**, **3a**, **5c**, and **6c**, respectively. Of diagnostic value for the β,γ-configuration in compounds of this type may be the size of $J(\beta,\gamma)$, inasmuch as it is larger (by ΔJ = 1.3 to 3.5 Hz, see *Table 2*) in the *arabino*- or *ribo*-isomers (**2** or **5**) than in the *xylo*- or *lyxo*-isomers (**3** or **6**).

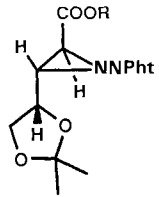
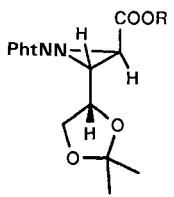
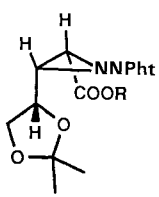
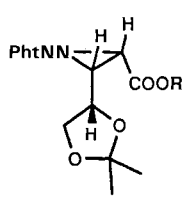
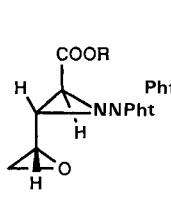
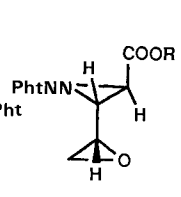
4. X-Ray Structure Analyses. – The results of the X-ray structure analyses of **2b**, **2d**, and **6a** are shown in the *Figure*[7])[8]). Each of these three compounds was the major isomer

[6]) We note that $J(\beta,\gamma)$ in the two stereoisomeric series **1** and **4** do not differ greatly (5.5–7.3 Hz). This suggests that the preferred conformation around the C(β)–C(γ) bond is either not strongly affected, or then rotated roughly around 180°, by the difference in interactions due to the *cis*- as compared to the *trans*-position of the ROOC group with respect to C(γ), even when R = *t*-Bu.

[7]) These results were obtained in our X-ray structure laboratory by Dr. *R. Prewo,* who expects to publish the details separately.

[8]) The optically active **6a** is known to have the (γS)-configuration from its synthesis.

Table 2. *Some Characteristic ^{1}H-NMR Data of the* arabino-, xylo-, ribo-, and lyxo-*Isomers* **2**, **3**, **5**, *and* **6**, *Respectively*[a])[b])

													
	arabino			*xylo*		*ribo*		*lyxo*		*arabino*		*xylo*	
	2a (R = Me)		**2b**[c]) (R = Et)	**3a** (R = Me)	**3b** (R = Et)	**5a** (R = Me)	**5c** (R = *t*-Bu)	**6a**[c]) (R = Me)	**6c** (R = *t*-Bu)	**2d**[c]) (R = Me)		**3d** (R = Me)	
	A	**B**[d])	**A**	**A**	**A**	**A**	**A**	**A**	**A**	**A**	**B**[e])	**A**	**B**[f])
δ (R) [ppm]	3.71	3.85	4.14, 1.28	3.69	4.13, 1.25	3.86	1.56	3.84	1.54	3.71	3.84	3.73	3.86
δ (H–C(α)) [ppm]	3.36		3.35	3.43	3.43	3.34	3.27	3.42	3.30	3.31	3.54	3.34	
$J(\alpha,\beta)$ [Hz]	4.8		4.8	4.9	5.0	8.2	8.3	8.5	8.5	4.9	5.1	5.0	
δ (H–C(β)) [ppm]	3.50		3.53	3.56	3.57	3.01	2.95	3.29	3.26	3.52	3.37	3.64	
$J(\beta,\gamma)$ [Hz]	6.9		7.0	3.4	3.5	8.2	8.4	6.9	6.5	4.5	1.8	2.9	
δ(H–C(γ)) [ppm]	4.06		4.06	4.53	4.54	4.32–4.24	4.27	4.44	4.44	3.27	3.47–3.46	3.39	
	(br. *q*)		(br. *q*)	(*ddd*)	(*ddd*)	(*m*)	(*m*)	(*q*)	(*q*)	(*ddd*)	(*m*)	(*ddd*)	
δ(H–C(δ)) [ppm]	4.42,		4.44,	4.29,	4.30,	4.69–4.63	4.34,	4.10,	4.08,	2.98,	2.81,	2.98,	
	4.28		4.29	4.22	4.24		4.50	4.00	3.91	2.90	2.55	2.92	

[a]) Measured in $CDCl_3$ at r.t.

[b]) **A** and **B** represent the invertomers at the aziridine N-atom, **A** being the major and **B** the minor one (see *Table 3*). Where only one invertomer is mentioned, only one was detected in the ^{1}H-NMR.

[c]) Structure confirmed by X-ray analysis.

[d]) **A**/**B** = 95:5.

[e]) **A**/**B** = 78:22.

[f]) **A**/**B** = 93:7.

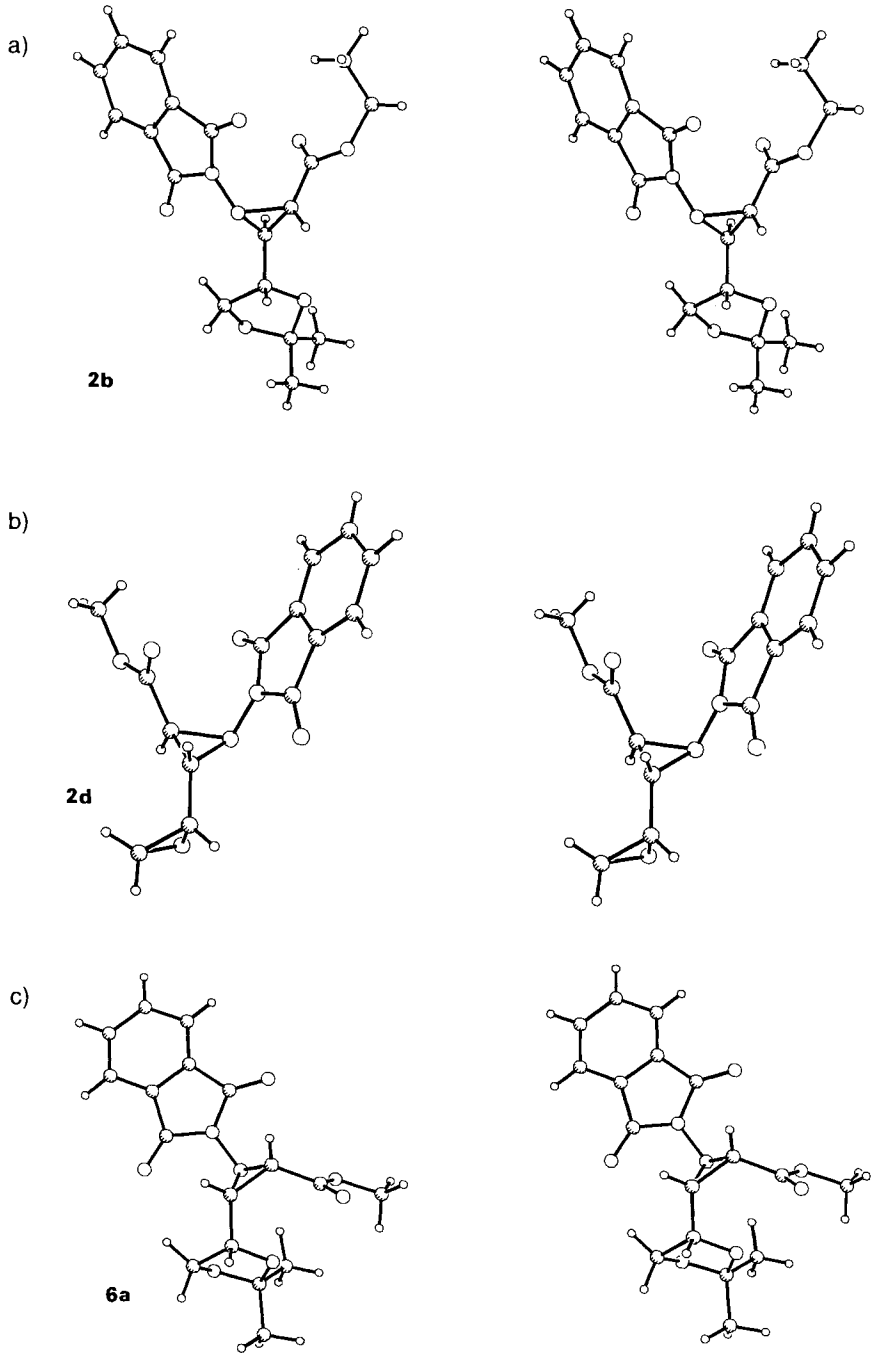


Figure. *Stereopictures of the X-ray structures of the aziridines* **2b**, **2d**, *and* **6a**. Only one enantiomer, namely the (*γS*)-form of racemic **2b** and **2d**, is shown.

(of two) obtained from an (*E*)-configurated dioxolanyl- (**1b**), from an (*E*)-configurated oxiranyl- (**1d**), and from a (*Z*)-configurated dioxolanyl derivative (**4a**), respectively. The X-ray analyses establish not only the constitution of these aziridines but also the *arabino*-configuration of **2b** and **2d** and the *lyxo*-configuration of **6a**. The *Figure* also shows the preferred conformations around the C(β)–C(γ) bond in the crystals of **2b**, **2d**, and **6a**, but correlations with the conformations in solutions, as expressed by the ^{1}H-NMR $J(\beta,\gamma)$ values, and of the latter with the β,γ-configurations is not immediately obvious[9]). In *Chapt. 5*, we shall show that the conformation at the C(β)–C(γ) bond may depend on the configuration at the stereogenic (pyramidal) aziridine N-atom.

The pyramidality and configuration at the aziridine ring N-atom is also revealed by the X-ray analyses: the PhtN substituent in the crystals of **2b**, **2d**, and **6a** is always *trans*-configurated with respect to the substructure around C(γ). Evidence for the generality of this effect in our samples will be presented in *Chapt. 5*.

5. Invertomers. – In $CDCl_3$ solution, the aziridine **2d** exists as two N-invertomers[10]), **2dA** and **2dB**, in the ratio of *ca.* 3:1; almost all ^{1}H-NMR signals of both invertomers can be seen separately (see *Table 3*). Freshly dissolved crystalline **2d** contained **2dA** and **2dB** in a *ca.* 10:1 ratio, which turned to *ca.* 3:1, the equilibrium, after a few minutes at r.t. Thus, the configuration at the aziridine N-atom of **2dA** corresponds to the one found in the crystal of **2d** (see the *Fig., b*), where the PhtN group is *trans*-configurated to the oxiranyl residue. Evidently, the PhtN residue is repulsed somewhat more by the oxiranyl group in **2d** than by the COOMe group. As noted by *Atkinson* and coworkers [18], a PhtN group on an aziridine magnetically shields the MeO protons of a *cis*-located vicinal COOMe group (3.68–3.70 ppm) more than those of a *trans*-located one (3.84–3.85 ppm), but it deshields vicinal protons in *cis*- more than in *trans*-position ($\Delta\delta$ = 0.4–0.6 ppm). Accordingly, we find in the ^{1}H-NMR spectrum of **2d** the MeO signal at 3.71 ppm for **2dA** *vs.* at 3.84 ppm for **2dB**, the H–C(α) signal at 3.31 ppm for **2dA** *vs.* at 3.54 ppm for **2dB**, and the H–C(β) signal at 3.52 ppm for **2dA** *vs.* at 3.37 ppm for **2dB**.

For **3d** and **2a**, a minor invertomer **B** (7% and 5%) could also be detected in the ^{1}H-NMR, besides the major **A** (see *Table 3*). Both **A**'s exhibit MeO signals at 3.73 and 3.71 ppm (COOMe/PhtN *cis* or C(γ)/PhtN *trans*), while both **B**'s absorb at 3.86 (7%) and 3.85 ppm (5%).

The methyl esters **3a**, **5a**, and **6a** appear to exist as only one invertomer, since only one MeO signal is visible (see *Table 3*). In the α,β-*trans*-aziridine **3a**, the MeO signal at 3.69 ppm indicates the COOMe/PhtN *cis*-relationship and thus identifies **3a** as the **A** invertomer. In the α,β-*cis*-aziridines **5a** and **6a**, on the other hand, the MeO signal is at 3.86 and 3.84 ppm, respectively, corresponding to a COOMe/PhtN *trans*-configuration and thus identifies **5a** and **6a** also as the **A** invertomers.

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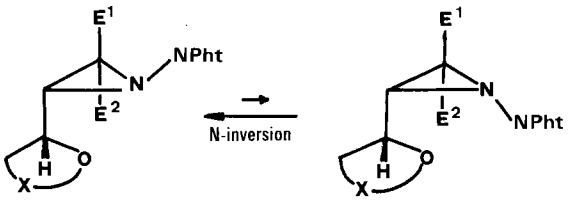
[9]) Of the two X-rayed *arabino*-aziridines with the larger $J(\beta,\gamma)$ values (**2b** 7.0, **2d** 4.9 Hz) as compared to their *ribo*-isomers (**3b** 3.5, **3d** 2.9 Hz), we find the H-atoms at C(β) and C(γ) in crystalline **2b** to be antiperiplanar (*Fig., a*), in crystalline **2d**, however, synclinal (*Fig., b*). The *lyxo*-aziridine **6a** with its synclinal H-atoms at C(β) and C(γ) in the crystal (*Fig., c*), on the other hand, exhibits a $J(\beta,\gamma)$ value (6.9 Hz) not so much smaller than its *ribo*-isomer **5a** (8.5 Hz).

[10]) The invertomers mentioned here are due to different pyramidal arrangements around the N-atom of the aziridine ring (see *Table 3*). The prefixes *cis* and *trans* refer to the relative positions of the PhtN group and the C(γ) substructure. The *trans*-invertomer, always the more abundant one, is called **A**, the *cis*-invertomer **B**.

Table 3. *^{1}H-NMR Signal* [ppm] *of the MeO Group in the N-Invertomers of the Methyl Aziridinecarboxylates* **2a**, **3a**, **2d**, **3d**, *and* **5a**



A (major) B (minor)

			A	B
α,β-*trans*-Series (E^1 = COOMe, E^2 = H)	**2a**	(X = $-OCMe_2-$)	3.71 (95%)	3.85 (5%)
	3a	(X = $-OCMe_2-$)	3.69 (100%)	none
	2d	(X = –)	3.71 (78%)	3.84 (12%)
	3d	(X = –)	3.73 (93%)	3.86 (7%)
α,β-*cis*-Series (E^1 = H, E^2 = COOMe)	**5a**	(X = $-OCMe_2-$)	3.86 (100%)	none
	6a	(X = $-OCMe_2-$)	3.84 (100%)	none

The greater repulsion exerted on the PhtN group by the substructure around C(γ) than by the COOMe group should also apply to the Et and *t*-Bu esters **2b**, **3b**, **5c**, and **6c**. Since they produce just one set of ^{1}H-NMR signals each, they should also exist as invertomer **A** only. This is supported for **5c** and **6c** by the chemical shifts of the *t*-Bu groups (1.54 and 1.56 ppm), which agree with the values given in [18] for the COO(*t*-Bu)/PhtN *trans*-invertomers of *N*-phthalimdoaziridines (1.53–1.56 ppm) but not with the corresponding *cis*-invertomers (1.33–1.38 ppm). The *Atkinson* effect is not visible with H–C(β) of our aziridines, possibly because it is obscured by conformational variances at the C(β)–C(γ) bond, as is suggested by the $J(\beta,\gamma)$ values shown in *Table 2*. Of interest in this connection is the difference in the $J(\beta,\gamma)$ values of the two invertomers of **2d** (4.5 for **A** and 1.8 Hz for **B**). Unfortunately, the $J(\beta,\gamma)$ values are not available for the invertomers **B** of our other aziridines.

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Experimental Part

General. See [10]. Reagent-grade solvents *(Fluka, Merck)* were dried over molecular sieves (3 Å, *Fluka*). $Pb(OAc)_4$ was freed from AcOH *in vacuo* at r.t. Anal. TLC: Al foil coated with silica gel *60 F (Merck)*; detection by UV (254 nm) or by spraying with 50% H_2SO_4 soln. followed by heating. GC: *Hewlett Packard 5880A* with capillary column *BP-5*, 25 m. M.p.: *Mettler FP 5*. $[\alpha]_D^T$: *Perkin Elmer 241* polarimeter, *c* in g/100 ml. ^{1}H-NMR spectra of enantiomerically pure compounds are described even though these data have already been reported for the racemic mixture, and *vice versa*, because it is known [19], that pure enantiomers and racemic mixtures do not need to exhibit exactly the same chemical shifts.

1. *Methyl (2E)- and (2Z)-3-[(4S)-2,2-Dimethyl-1,3-dioxolan-4-yl]prop-2-enoate* (**1a** and **4a**, resp.). 1.1. *In* CH_2Cl_2. As described in [20] [21] for the racemic mixture, **1a**/**4a** were prepared from (*R*)-2,3-*O*-isopropylideneglyceraldehyde and [(methoxycarbonyl)methylidene]triphenylphosphorane in CH_2Cl_2 as a crude 4:1 mixture (GC). *Lobar* chromatography (AcOEt/hexane 15:85) afforded **1a** (65%) and **4a** (17%), both as colorless oils, each > 98% pure by GC.

Data of **1a**: $[\alpha]_D^{25} = +45$ ($c = 1.125$, $CHCl_3$; [6j]: +33.6° ($c = 10$, $CDCl_3$)). ^{1}H-NMR (J(H–C(2),H–C(3)) = 16.5 Hz) and IR: identical with those of the (2*E*)-isomer **1a** reported in [6j].

Data of **4a**: $[\alpha]_D^{25} = +122$ ($c = 1.25$, $CHCl_3$). IR: identical with that of the racemic mixture [21]. ^{1}H-NMR (200 MHz, $CDCl_3$): 6.38 (*dd*, $J = 11.6$, 6.6, H–C(3)); 5.86 (*dd*, $J = 11.6$, 1.7, H–C(2)); 5.50 (*dddd*, $J = 6.9$, 6.7, 6.6, 1.7, H–C(4′)); 4.39 (*dd*, $J = 8.3$, 6.9, H–C(5′)); 3.72 (*s*, MeO); 3.62 (*dd*, $J = 8.3$, 6.7, H–C(5′)); 1.46, 1.40 (2 *s*, $Me_2C(2')$). ([21]: ^{1}H-NMR of the racemic mixture).

To determine the optical purity of **1a** and **4a**, a sample of the crude 4:1 mixture **1a**/**4a** was analyzed on a *Carlo Erba Fractovap G 1* (cap. column *WCOT, XE-60-*(*S*)-valine-[(*S*)-α-phenylethyl]amide). Only one peak was found for each of the two olefins. A calibration of the column using different mixtures of **1a** and the corresponding racemic material showed **1a** to have ee > 98%. Since it is highly improbable that **4a**, formed in the same reaction pot, has racemized to a larger extent, it is assumed to have the same optical purity.

1.2. *In MeOH.* The same *Wittig* reaction with (*R*)-2,3-*O*-isopropylideneglyceraldehyde was also run in MeOH, as described in [21]. It afforded a crude 1:4 mixture **1a**/**4a**. After chromatography on *Lobar* (AcOEt/hexane 15:85) **1a** (14%) and **4a** (61%), each > 98% pure by GC, were obtained, with the same properties as described in *Exper. 1.1.*

2. *Ethyl (2*E*)-3-[(4*RS*)-2,2-Dimethyl-1,3-dioxolan-4-yl]prop-2-enoate* (**1b**). Using the procedure described in [22] for the methyl ester, *ethyl (4*RS*,2*E*)-4,5-dihydroxypent-2-enoate* was prepared from *rac*-glyceraldehyde and [(ethoxycarbonyl)methylidene]triphenylphosphorane in 80% yield as a colorless oil. B.p. 130°/0.1 Torr. IR (film): 3400*s*, 2985*m*, 2940*m*, 2880*m*, 1785 (sh), 1745 (sh), 1722 (*sh*), 1708*s*, 1660*m*, 1395*m*, 1371*s*, 1308*s*, 1280*s*, 1180*s*, 1125*m*, 1075*m*, 1035*s*, 980*m*, 885*m*, 865*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 6.91 (*dd*, $J = 15.8$, 4.5, H–C(3)); 6.15 (*dd*, $J = 15.8$, 1.8, H–C(2)); 4.42 (*m*, H–C(4)); 4.22 (*q*, $J = 7.0$, CH_3CH_2O); 3.78 (*dd*, $J = 11.0$, 3.5, H–C(5)); 3.54 (*dd*, $J = 11.0$, 7.0, H–C(5)); 2.95 (*s*, 2 OH); 1.30 (*t*, $J = 7.0$, CH_3CH_2O). Anal. calc. for $C_7H_{12}O_4$ (160.17): C 52.49, H 7.55; found: C 52.77, H 7.76.

A soln. of ethyl (4*RS*,2*E*)-4,5-dihydroxypent-2-enoate (1600 mg, 10 mmol), acetone (7.35 ml, 100 mmol) and TsOH (5 mg, 0.025 mmol) in benzene (40 ml) was heated to reflux for 12 h under azeotropic removal of H_2O. Powdered K_2CO_3 was added, the suspension stirred for few min and filtered. Distillation of the residue after evaporation of the solvent yielded 1600 mg (80%) **1b** as a colorless oil, > 99% pure by GC. B.p. 145°/15 Torr. IR: identical with the spectrum of the optically active compound described in [23]. ^{1}H-NMR (200 MHz, $CDCl_3$): 6.88 (*dd*, $J = 15.6$, 5.6, H–C(3)); 6.08 (*dd*, $J = 15.6$, 1.4, H–C(2)); 4.66 (*dddd*, $J = 7.1$, 6.5, 5.6, 1.4, H–C(4′)); 4.21 (*q*, $J = 7.1$, CH_3CH_2O); 4.19 (*dd*, $J = 8.2$, 6.5, H–C(5′)); 3.68 (*dd*, $J = 8.2$, 7.1, H–C(5′)); 1.45, 1.41 (2 *s*, $Me_2C(2')$); 1.30 (*t*, $J = 7.1$, CH_3CH_2O); no signals of the (2*Z*)-isomer (J(H–C(2),H–C(3)) = 12 Hz) as described for the (*R*)-enantiomer in [24].

3. tert-*Butyl (2*E*)- and (2*Z*)-3-[(4*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl]prop-2-enoate* (**1c** and **4c**, resp.). In analogy to the method described in *Exper. 1.2,* **1c** and **4c** were prepared from (*R*)-2,3-*O*-isopropylideneglyceraldehyde and {[(*tert*-butoxy)carbonyl]methylidene}triphenylphosphorane [25] in MeOH in 11% and 82% yield, respectively, after chromatography, as colorless oils, each > 98% pure by ^{1}H-NMR and GC. The optical purities of **1c** and **4c** are assumed to be > 98% as in **1a** and **4a** (see *Exper. 1.1*), since the same starting material was used in the same type of reaction.

Data of **1c**: IR (film): 2985*s*, 2935*m*, 2875*m*, 1715*s*, 1660*m*, 1455*m*, 1393*m*, 1382*m*, 1370*s*, 1311*s*, 1260*s*, 1155*s*, 1065*s*, 980*m*, 850*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 6.78 (*dd*, $J = 15.6$, 5.9, H–C(3)); 6.01 (*dd*, $J = 15.6$, 1.4, H–C(2)); 4.64 (*dddd*, $J = 7.2$, 6.5, 5.9, 1.4, H–C(4′)); 4.17 (*dd*, $J = 8.3$, 6.5, H–C(5′)); 3.66 (*dd*, $J = 8.3$, 7.2, H–C(5′)); 1.48 (*s*, *t*-Bu); 1.45, 1.40 (2 *s*, $Me_2C(2')$).

Data of **4c**: $[\alpha]_D^{25} = +97$ ($c = 1.047$, $CHCl_3$). IR (film): 2985*s*, 2935*m*, 2875*m*, 1713*s*, 1644*m*, 1455*m*, 1408*m*, 1381*m*, 1370*s*, 1235*s*, 1216*s*, 1158*s*, 1061*s*, 855*m*, 822*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 6.25 (*dd*, $J = 11.7$, 6.7, H–C(3)); 5.77 (*dd*, $J = 11.7$, 1.7, H–C(2)); 5.50 (*dddd*, $J = 6.9$, 6.8, 6.7, 1.7, H–C(4′)); 4.37 (*dd*, $J = 8.3$, 6.9, H–C(5′)); 3.62 (*dd*, $J = 8.3$, 6.8, H–C(5′)); 1.48 (*s*, *t*-Bu); 1.45, 1.39 (2*s*, $Me_2C(2')$). Anal. calc. for $C_{12}H_{20}O_4$ (228.23): C 63.14, H 8.83; found: C 63.39, H 8.70.

4. *Methyl (2*E*)-3-[(2*RS*)-oxiran-2-yl]prop-2-enoate* (**1d**) was prepared by epoxidation of methyl (2*E*)-penta-2,4-dienoate (commercial material, 77% pure by GC, containing 8% of the (2*Z*)-isomer, 10% of an unknown compound and some other impurities) as described in [21]. Separation on *Lobar* (AcOEt/hexane 15:85) and distillation at 100°/20 Torr, with some loss for the sake of purity, afforded **1d** (18%) as a colorless oil, > 99% pure by GC. ^{1}H-NMR (J(H–C(2),H–C(3)) = 16 Hz) and IR: identical with those described in [21], the ^{1}H-NMR showed none of the (2*Z*)-isomer (see below).

One *Lobar* fraction, after repeated chromatography (*Lobar*, AcOEt/hexane 15:85) and distillation, yielded a small amount (< 1%) of *methyl (2Z)-3-[(2*RS*)-oxiran-2-yl]prop-2-enoate* (**4d**) as a colorless oil, > 90% pure by GC. ^{1}H-NMR (J(H–C(2),H–C(3)) = 10 Hz) and IR: identical with those of the (2*Z*)-isomer described in [21].

5. *Methyl (2*S,*3*S*)- and (2*R,*3*R*)-3-[(4*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl]-1-phthalimidoaziridine-2-carboxylate* (**2a** and **3a**, resp.). 5.1. *At 0°*. To a stirred mixture of **1a** (640 mg, 3.5 mmol; > 98% pure), *N*-aminophthalimide (680 mg, 4.2 mmol), and Na_2CO_3 (740 mg, 7 mmol) in CH_2Cl_2 (8 ml) at 0°, $Pb(OAc)_4$ (1860 mg, 4.2 mmol) was added within 0.5 h. After removing the cooling bath and further stirring for 0.5 h, the solid was filtered off and washed with CH_2Cl_2. The combined washings and filtrate were evaporated to dryness and the residue chromatographed on *Lobar B* (AcOEt/hexane 3:7), yielding 250 mg (39%) of **1a** and 700 mg (59%) of a 3.1:1 mixture (by ^{1}H-NMR) **2a**/**3a**. Crystallization from hexane/acetone 3:1 afforded 145 mg (12%) **2a**. M.p. 150–152° after recrystallization from the same solvent, as light green needles. M.p. 153.2–153.6°. $[\alpha]_D^{25} = -99$ ($c = 0.995$, $CHCl_3$). In soln., the two invertomers **A** (major) and **B** (minor) were present. IR ($CHCl_3$): 3020*w*, 2990*w*, 1770*w*, 1720*s*, 1610*w*, 1450*m*, 1380*s*, 1200*m* (br.), 1070*s*, 890*m*, 840*m*, 700*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.78–7.72, 7.68–7.63 (2 *m*, 4 arom. H); 4.42 (*dd*, J = 8.8, 5.9, H–C(5′)); 4.28 (*dd*, J = 8.8, 6.2, H–C(5′)); 4.06 (br. *q*, J = 5.9–6.9, H–C(4′)); 3.85 (*s*, 0.15 H, MeO of invertomer **B**); 3.71 (*s*, 2.85 H, MeO of invertomer **A**); 3.50 (*dd*, J = 6.9, 4.8, H–C(3)); 3.36 (*d*, J = 4.8, H–C(2)); 1.48, 1.40 (2 *s*, $Me_2C(2')$). MS (70 eV): 346 (1, $M^{+\cdot}$), 331 (23), 287 (12), 239 (11), 229 (37), 221 (17), 213 (15), 201 (24), 148 (12), 130 (22), 104 (76), 101 (80), 76 (46), 43 (100). Anal. calc. for $C_{17}H_{18}N_2O_6$ (346.34): C 58.96, H 5.24, N 8.09; found: C 59.11, H 5.39, N 8.24.

The ^{1}H-NMR of **3a** was obtained by subtracting the spectrum of **2a** from that of the mother-liquor material (*ca.* 1:1 mixture **2a**/**3a**). ^{1}H-NMR (400 MHz, $CDCl_3$) of **3a**: 7.78–7.71 (*m*, 2 arom. H); 7.69–7.63 (*m*, 2 arom. H); 4.53 (*ddd*, J = 6.6, 5.5, 3.4, H–C(4′)); 4.29 (*dd*, J = 8.8, 5.5, H–C(5′)); 4.22 (*dd*, J = 8.8, 6.6, H–C(5′)); 3.69 (*s*, MeO); 3.56 (*dd*, J = 4.9, 3.4, H–C(3)); 3.43 (*d*, J = 4.9, H–C(2)); 1.41, 1.35 (2*s*, $Me_2C(2')$).

5.2. *At −40°*. The same reaction at −40° (instead of 0°) yielded 59% of **2a**/**3a** in a ratio of 30:1, in addition to 31% of **1a**. The amount of **3a** was determined by ^{1}H-NMR of the mother-liquor material after chromatographic removal of **1a** and crystallization of the bulk of the major product **2a**.

6. *Ethyl (2*RS,*3*RS*)- and (2*SR,*3*SR*)-3-[(4*RS*)-2,2-Dimethyl-1,3-dioxolan-4-yl]-1-phthalimidoaziridine-2-carboxylate* (**2b** and **3b**, resp.). 6.1. *At 0°*. The reaction of **1b** (700 mg, 3.5 mmol; > 99% pure), *N*-aminophthalimide (680 mg, 4.2 mmol), Na_2CO_3 (740 mg), and $Pb(OAc)_4$ (1860 mg, 4.2 mmol) in CH_2Cl_2 (8 ml) at 0°, following the procedure described in *Exper. 5*, yielded 270 mg (39%) of **1b** and 760 mg (60%) of a 3.3:1 mixture (by ^{1}H-NMR) **2b**/**3b**. Crystallization from hexane/acetone 3:1 afforded 175 mg (14%) of **2b**. M.p. 130–131°. After recrystallization from the same solvent as light-green needles. M.p. 130.5–131.5°. A sample of these crystals was used for X-ray analysis. IR ($CHCl_3$): 2990*w*, 1770*w*, 1720*s*, 1380*s*, 1220*m*, 1070*m*, 890*m*. ^{1}H-NMR (400 MHz: $CDCl_3$): 7.79–7.66 (*m*, 4 arom. H); 4.44 (*dd*, J = 8.7, 5.9, H–C(5′)); 4.29 (*dd*, J = 8.7, 6.2, H–C(5′)); 4.14 (*m*, CH_3CH_2O); 4.06 (br. *q*, J = 5.9–7.0, H–C(4′)); 3.53 (*dd*, J = 7.0, 4.8, H–C(3)); 3.35 (*d*, J = 4.8, H–C(2)); 1.49, 1.40 (2 *s*, $Me_2C(2')$); 1.28 (*t*, J = 7.1, CH_3CH_2O). MS (70 eV): 345 (6, $M^{+\cdot} - 15$), 229 (20), 213 (26), 201 (19), 104 (60), 101 (52), 76 (41), 43 (100). Anal. calc. for $C_{18}H_{20}N_2O_6$ (360.37): C 59.99, H 5.59, N 7.77; found: C 60.00, H 5.65, N 7.85.

The ^{1}H-NMR of **3b** was obtained by subtracting the spectrum of **2b** from that of the mother-liquor material (*ca.* 1:1 mixture **2b**/**3b**). ^{1}H-NMR (400 MHz, $CDCl_3$) of **3b**: 7.77–7.65 (*m*, 4 arom. H); 4.54 (*ddd*, J = 6.5, 5.7, 3.5, H–C(4′)); 4.30 (*dd*, J = 8.7, 5.7, H–C(5′)); 4.24 (*dd*, J = 8.7, 6.5, H–C(5′)); 4.13 (*q*, J = 7.1, CH_3CH_2O); 3.57 (*dd*, J = 5.0, 3.5, H–C(3)); 3.43 (*d*, J = 5.0, H–C(2)); 1.43, 1.37 (2 *s*, $Me_2C(2')$); 1.25 (*t*, J = 7.1, CH_3CH_2O).

6.2. *At −38°*. The same reaction at −38° (instead of 0°) yielded 59% **2b**/**3b** in a ratio 290:1, in addition to 38% of **1b**. The amount of **3b** was determined by ^{1}H-NMR of the mother-liquor material after chromatographic removal of **1b** and crystallization of the bulk of the major product **2b**.

7. *Methyl (2*RS,*3*RS*)-3-[(2*RS*)- and (2*SR*)-Oxiran-2-yl]-1-phthalimidoaziridine-2-carboxylate* (**2d** and **3d**, resp.). The reaction of **1d** (365 mg, 2.8 mmol; > 99% pure), *N*-aminophthalimide (505 mg, 3.1 mmol), Na_2CO_3 (740 mg, 7 mmol), and $Pb(OAc)_4$ (1382 mg, 3.1 mmol) in CH_2Cl_2 (8 ml) at 0°, following the procedure described in *Exper. 5*, yielded, after *Lobar B* (AcOEt/hexane 1:1), 92 mg (25%) of **1d** and 490 mg (54%) of a 2:1 mixture **2d**/**3d** as a highly viscous yellow oil containing *ca.* 9% of AcOEt (by ^{1}H-NMR). Repeated recrystallization from AcOEt/hexane 2:3 afforded **2d** as yellow prisms. M.p. 120°–121°. A sample of these crystals was used for X-ray analysis. The crystalline material **2d** contained only the invertomer **A** (see *Figure, c*); in soln. both **A** (major) and **B** (minor) were present. IR ($CHCl_3$): 3000*m*, 2960*w*, 1785*w*, 1770*w*, 1725*s*, 1610*w*, 1380*m*. ^{1}H-NMR (400 MHz, $CDCl_3$) of **2dA**/**2dB**: 7.82–7.66 (*m*, 4 arom. H); 3.84 (*s*, 0.65 H, MeO of **2dB**); 3.71 (*s*, 2.35 H, MeO of **2dA**); 3.54 (*d*, J = 5.1, 0.25 H, H–C(2) of **2dB**); 3.52 (*dd*, J = 4.5, 4.9, 0.75 H, H–C(3) of **2dA**); 3.47–3.46

(*m*, 0.25 H, H–C(2′) of **2dB**); 3.37 (*dd*, *J* = 5.1, 1.8, 0.25 H, H–C(3) of **2dB**); 3.31 (*d*, *J* = 4.9, 0.75 H, H–C(2) of **2dA**); 3.27 (*ddd*, *J* = 4.5, 4.0, 2.5, 0.75 H, H–C(2′) of **2dA**); 2.98 (*dd*, *J* = 5.1, 4.0, 0.75 H, H–C(3′) of **2dA**); 2.90 (*dd*, *J* = 5.1, 2.5, 0.75 H, H–C(3′) of **2dA**); 2.81 (*dd*, *J* = 5.1, 4.1, 0.25 H, H–C(3′) of **2dB**); 2.55 (*dd*, *J* = 5.1, 2.5, 0.25 H, H–C(3′) of **2dB**). MS (70 eV): 288 (1, $M^{+\cdot}$), 229 (9, $M^{+\cdot} - CO_2Me$), 201 (7), 173 (6), 130 (11), 105 (21), 104 (100). Anal. calc. for $C_{14}H_{12}N_2O_5$ (288.26): C 58.33, H 4.20, N 9.72; found: C 58.34, H 4.12, N 9.94. ^{1}H-NMR (80 MHz, $CDCl_3$): immediately after dissolving a few crystals of **2d**: 3.84 (*s*, 0.30 H); 3.71 (*s*, 2.70 H); after 2 min: 3.84 (*s*, 0.65 H); 3.71 (*s*, 2.35 H).

The ^{1}H-NMR of **3d** was obtained by subtracting the spectrum of **2d** from that of the mother-liquor material (*ca.* 1:5 mixture **2d**/**3d**). In this soln. the invertomers **A** (major) and **B** (minor) were present. ^{1}H-NMR (400 MHz, $CDCl_3$) of **3d**: 7.78–7.64 (*m*, 4 arom. H); 3.86 (*s*, 0.2 H, MeO of invertomer **3dB**): 3.73 (*s*, 2.8 H, MeO of invertomer **3dA**); 3.64 (*dd*, *J* = 5.0, 2.9, H–C(3)); 3.39 (*ddd*, *J* = 4.0, 2.9, 2.6, H–C(2′)); 3.34 (*d*, *J* = 5.0, H–C(2)); 2.98 (*dd*, *J* = 5.2, 2.6, H–C(3′)); 2.92 (*dd*, *J* = 5.2, 4.0, H–C(3′)).

8. *Methyl (2*R*,3*S*)- and (2*S*,3*R*)-3-[(4*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl]-1-phthalimidoaziridine-2-carboxylate* (**5a** and **6a**, resp.). 8.1. *At 0°*. The reaction of **4a** (3500 mg, 18.8 mmol; > 98% pure), *N*-aminophthalimide (3.35 g, 20.7 mmol), Na_2CO_3 (4000 mg, 38 mmol), and $Pb(OAc)_4$ (9200 mg, 20.7 mmol) in CH_2Cl_2 (40 ml) at 0°, following the procedure described in *Exper. 5*, yielded, after *Lobar B* (AcOEt/hexane 7:13), 2350 mg (67%) of **4a**, 610 mg (9%) of **5a**, and 750 mg (12%) of **6a**, all pure by ^{1}H-NMR. A sample of **5a** and **6a** each was further purified by crystallization.

Data of **5a**: colorless needles from acetone/hexane. M.p. 131–134°. $[\alpha]_D^{25} = +3$ (*c* = 1.085, $CHCl_3$). IR ($CHCl_3$): 3000*m*, 1780*m*, 1750*s*, 1720*s*, 1470*m*, 1440*m*, 1370*s*, 1200*m*, 1150*m*, 1070*s*, 910*m*, 840*m*, 710*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.79–7.74, 7.73–7.66 (2 *m*, 4 arom. H); 4.69–4.63 (*m*, H–C(5′)); 4.32–4.24 (*m*, H–C(5′), H–C(4′)); 3.86 (*s*, MeO); 3.34 (*d*, *J* = 8.2, H–C(2)); 3.01 (*t*[4.28 → *d*], *J* = 8.2, H–C(3)); 1.48, 1.36 (2 *s*, $Me_2C(2')$). MS (70 eV): 331 (20, $M^{+\cdot} - 15$), 270 (11), 239 (13), 229 (53), 201 (32), 130 (27), 104 (65), 101 (24), 76 (52), 43 (100). Anal. calc. for $C_{17}H_{18}N_2O_6$ (346.34): C 58.96, H 5.24, N 8.09; found: C 59.24, H 5.24, N 8.05.

Data of **6a**: colorless needles from $(i\text{-Pr})_2O$. M.p. 88.2–89.2°. $[\alpha]_D^{25} = -40$ (*c* = 1.005, $CHCl_3$). A sample of these crystals was used for X-ray analysis. IR ($CHCl_3$): 3000*m*, 2950*w*, 1780*m*, 1730*s*, 1610*w*, 1470*m*, 1440*m*, 1370*s*, 1200*m*, 1150*m*, 1070*s*, 950*m*, 840*m*, 700*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.80–7.70 (*m*, 4 arom. H); 4.44 (*q*, *J* = 6.6, H–C(4′)); 4.10 (*dd*, *J* = 8.6, 6.6, H–C(5′)); 4.00 (*dd*, *J* = 8.6, 6.1, H–C(5′)); 3.84 (*s*, MeO); 3.42 (*d*, *J* = 8.5, H–C(2)); 3.29 (*dd*, *J* = 8.5, 6.9, H–C(3)); 1.53, 1.38 (2 *s*, $Me_2C(2')$). MS (70 eV): 331 (17, $M^{+\cdot} - 15$), 239 (18), 229 (40), 201 (20), 130 (23), 111 (21), 104 (68), 101 (66), 76 (53), 43 (100). Anal. calc. for $C_{17}H_{18}N_2O_6$ (346.34): C 58.96, H 5.24, N 8.09; found: C 58.88, H 5.30, N 8.33.

8.2. *At −40°*. The same reaction at −40° (instead of 0°) yielded only 4% of **5a** and 8% of **6a**, in addition to 81% of **4a**.

9. tert-*Butyl (2*R*,3*S*)- and (2*S*,3*R*)-3-[(4*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl]-1-phthalimidoaziridine-2-carboxylate* (**5c** and **6c**, resp.). The reaction of **4c** (890 mg, 3.9 mmol; > 98% pure), *N*-aminophthalimide (820 mg, 5 mmol), Na_2CO_3 (830 mg, 7.8 mmol), and $Pb(OAc)_4$ (2250 mg, 5.1 mmol) in CH_2Cl_2 (9 ml) at 0°, following the procedure described in *Exper. 5*, yielded, after *Lobar B* (AcOEt/hexane 1:3), 470 mg (53%) of **4c**, 160 mg (11%) of **5c**, and 160 mg (11%) of **6c**, all pure by ^{1}H-NMR. A sample of **5c** and **6c** each was further purified by crystallization.

Data of **5c**: colorless needles from hexane/acetone. M.p. 180.5–182.0°. $[\alpha]_D^{25} = +11$ (*c* = 1.005, $CHCl_3$). IR (KBr): 2990*m*, 2940*w*, 1770*m*, 1720*s*, 1610*w*, 1470*w*, 1400*m*, 1380*s*, 1230*s*, 1160*s*, 1100*m*, 1050*s*, 910*m*, 840*m*, 710*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.80–7.70 (*m*, 4 arom. H); 4.59 (*dd*, *J* = 8.6, 5.4 [4.27], H–C(5′)); 4.34 (*dd*, *J* = 8.6, 6.1 [4.27], H–C(5′)); 4.27 (*m* [2.95 → *t*, *J* = 6,0], H–C(4′)); 3.27 (*d*, *J* = 8.3 [2.95], H–C(2)); 2.95 (*t* [4.27 → *d*], *J* = 8.4, H–C(3)); 1.56 (*s*, *t*-Bu); 1.48, 1.35 (2 *s*, $Me_2C(2')$). MS (70 eV): 373 (1, $M^{+\cdot} - 15$), 317 (12), 229 (21), 213 (24), 201 (10), 162 (12), 148 (17), 130 (15), 104 (42), 101 (17), 76 (30), 57 (100). Anal. calc. for $C_{20}H_{24}N_2O_6$ (388.42): C 61.85, H 6.28, N 7.21; found: C 61.58, H 6.03, N 7.47.

Data of **6c**: colorless fine needles from hexane/acetone. M.p. 143–145°. $[\alpha]_D^{25} = -28$ (*c* = 1.025, $CHCl_3$). IR (KBr): 2990*m*, 2930*w*, 1780*m*, 1730*s*, 1470*w*, 1380*s*, 1230*s*, 1160*s*, 1070*s*, 920*m*, 850*m*, 700*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.80–7.70 (*m*, 4 arom. H); 4.44 (*q* [3.28 → *t*], *J* = 6.5, H–C(4′)); 4.08 (*dd*, *J* = 8.4, 6.8 [4.44], H–C(5′)); 3.91 (*dd*, *J* = 8.4, 6.1 [4.44], H–C(5′)); 3.31–3.24 (*m*, 2 H [4.44 → 3.30 (*d*, *J* = 8.5, H–C(2)) and 3.26 (*dd*, *J* = 8.5, 6.5, H–C(3))]); 1.54 (*s*, *t*-Bu); 1.56, 1.41 (2 *s*, $Me_2C(2')$). MS (70 eV): 373 (1, $M^{+\cdot} - 15$), 317 (31), 257 (12), 229 (26), 213 (20), 201 (19), 162 (15), 148 (23), 147 (26), 130 (20), 104 (70), 101 (60), 76 (59), 57 (100), 43 (90). Anal. calc. for $C_{20}H_{24}N_2O_6$ (388.42): C 61.85, H 6.28, N 7.21; found: C 61.72, H 6.01, N 7.15.

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