5: To a solution of **4** (2.97 g, 6.8 mmol) in benzene (20 mL) was added dropwise a solution of $LiN(SiMe_3)_2$ (1.14 g, 6.8 mmol) in benzene (30 mL). After being stirred for 14 h the mixture was filtered, and the solvent was condensed off. The yellow-brown oil obtained crystallized after 12 h. Recrystallization from hexane gave 2.37 g (62%) of light yellow crystals. Correct elemental analysis; ^{1}H NMR: $\delta = 0.50$ (s, 18H, $N(SiMe_3)_2$), 0.71 (s, 3H, SiMe), 1.13 (s, 18H, N*t*Bu), 1.28 (s, 9H, N*t*Bu), 5.67 (s, 2H, CH) $^5J(^1H, ^{117/119}Sn) = 5.6$ Hz; ^{13}C NMR: $\delta = 7.59$ (s, $N(SiMe_3)_2$), 9.21 (s, SiMe), 29.71 (s, $NC(CH_3)_3$), 35.50 (s, $NC(CH_3)_3$), 52.26 (s, $NC(CH_3)_3$), 54.74 (s, $NC(CH_3)_3$), 118.15 (s, *C*H); ^{15}N NMR: $\delta = -289.8$ (s, N*t*Bu); ^{29}Si NMR: $\delta = -15.70$ (s, SiMe, $^2J(^{29}Si, ^{117/119}Sn) = 20.6$ Hz), -0.77 (s, $N(SiMe_3)_2$, $^2J(^{29}Si, ^{117/119}Sn) = 54.4/19.2$ Hz); ^{119}Sn NMR: $\delta = 205.2$ (s, NSnN, $b_{1/2} = 774$ Hz).

6: To a solution of **5** (0.258 g, 0.459 mmol) in benzene (20 mL) was added dropwise phenyl azide (0.109 g,0.919 mmol). The solution rapidly turned red with the evolution of gas. After the mixture was stirred for 2 h the solvent was removed, and the residue recrystallized from hexane to give 0.27 g (78%) of light yellow crystals. Correct elemental analysis; ^{1}H NMR: $\delta = 0.14$ (s, 18H, $N(SiMe_3)_2$), 0.77 (s, 3H, SiMe), 1.17 (s, 18H, N*t*Bu), 1.56 (s, 9H, N*t*Bu), 5.42 (s, 2H, CH, $^3J(^1H, ^{117/119}Sn) = 57.8/60.4$ Hz), 6.85 – 7.26 (m, 10H, C_6H_5); ^{13}C NMR: $\delta = 4.97$ (s, $N(SiMe_3)_2$, $^3J(^{13}C, ^{117/119}Sn) = 28.0$ Hz), 8.89 (s, SiMe, $^3J(^{13}C, ^{117/119}Sn) = 15.9$ Hz), 31.95 (s, $NC(CH_3)_3$), 36.92 (s, $NC(CH_3)_3$, $^3J(^{13}C, ^{117/119}Sn) = 15.3$ Hz), 52.48 (s, $NC(CH_3)_3$), 54.95 (s, $NC(CH_3)_3$, $^2J(^{13}C, ^{117/119}Sn) = 14.4$ Hz), 79.37 (s, CH, $^2J(^{13}C, ^{117/119}Sn) = 15.9$ Hz), 121.20 (s, NC_6H_5, $^5J(^{13}C, ^{117/119}Sn) = 4.7$ Hz), 125.57 (s, NC_6H_5, $^4J(^{13}C, ^{117/119}Sn) = 12.3$ Hz), 128.49 (s, NC_6H_5), 152.29 (s, NC_6H_5, $^2J(^{13}C, ^{117/119}Sn) = 8.3$ Hz); ^{15}N NMR: $\delta = -270.3$ (s, N*t*Bu), -294.9 (s, N*t*Bu), -336.2 (s, NC_6H_5); ^{29}Si NMR: $\delta = -8.33$ (s, SiMe, $^2J(^{29}Si, ^{117/119}Sn) = 22.4$ Hz), 8.37 (s, $N(SiMe_3)_2$, $^2J(^{29}Si, ^{117/119}Sn) = 28.0/7.4$ Hz); ^{119}Sn NMR: $\delta = -175.3$ (s, NSnN).

Received: June 29, 1998 [Z12063]
German version: *Angew. Chem.* **1999**, *111*, 131 – 134

Keywords: carbene analogues · cage compounds · multicomponent reactions · nitrenes · nitrogen heterocycles

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N,N-Phthaloylamino Acids as Chiral Auxiliaries in Asymmetric Mannich-Type Reactions**

Roland Müller, Helmut Goesmann, and Herbert Waldmann*

Dedicated to Professor Janos Rétey on the occasion of his 65th birthday

The Mannich reaction is one of the most important methods of organic synthesis. It provides a powerful tool for instance for the construction of β-amino ketones and β-amino acids that are versatile building blocks in the preparation of biologically important compounds[1] and their analogues (for example β-peptides[2]). Therefore, the development of methods that allow this transformation to be carried out asymmetrically is of great importance to organic synthesis, and diastereo-[3] and enantioselective[3a, 4] Mannich-type processes have attracted considerable attention. Herein we report that a very high level of stereoselectivity (diastereomeric ratio of

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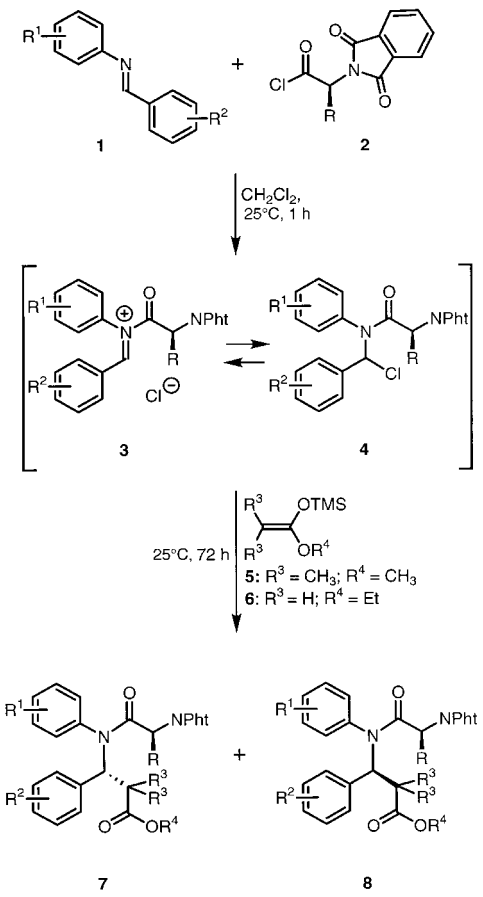
[**] This research was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

  1433-7851/99/3801-0184 $ 17.50+.50/0

more than 99:1) is reached in Mannich-type reactions with *N*,*N*-phthaloylamino acids as removable chiral auxiliary groups.

If Schiff bases **1** are treated with *N*,*N*-phthaloyl-protected amino acid chlorides[5] **2** and the silylketene acetals **5** or **6** at room temperature the N-acylated β-amino acid esters **7** and **8** are formed in a smooth reaction in moderate to high yields and with good to excellent diastereomer ratios (Scheme 1, Table 1). Presumably the reaction proceeds by the attack of



Scheme 1. Asymmetric Mannich reactions with *N*,*N*-phthaloylamino acids as the chiral auxiliaries.

the acid chlorides on the nitrogen atom of the C=N bond to give rise to N-acyliminium intermediates **3**, which are then attacked by the nucleophile **5** or **6** at the electrophilic carbon atom of the C=N bond. We assume that prior to the nucleophilic attack the *Z*-imines **1** are converted into the *E*-iminium salts **3** by the addition and re-elimination of the chloride ion, that is by intermediary formation of chloroalkylamides **4**.[6] Unfavorable steric interactions between the amino acid side chain (or the N-phthaloyl (NPht) group) and the aryl group linked to the imine carbon atom are thereby avoided (Scheme 1).

In a first series of experiments with the silylketene acetal **5** the factors that influence the efficiency of the stereoselection were determined. The stereoselectivity increases with an increase in the steric demand of the amino acid side chain, with Pht-alanine and Pht-valine being clearly less favorable auxiliaries than Pht-*tert*-leucine (Table 1, entries 1–3). The

Table 1. Results of the Mannich reactions with *N*,*N*-phthaloyl amino acids as chiral auxiliary groups to give the β-amino acid esters **7** and **8**.

Entry	7	R	R^1	R^2	R^3	R^4	Yield [%][a]	7:8[b]
1	**a**	CH_3	H	H	Me	Me	67	78:22
2	**b**	*i*Pr	H	H	Me	Me	80	87:13
3	**c**	*t*Bu	H	H	Me	Me	54	93:7
4	**d**	*t*Bu	H	4-MeO	Me	Me	84	91:9
5	**e**	*t*Bu	H	2-MeO	Me	Me	91	92:8
6	**f**	*t*Bu	H	4-NMe_2	Me	Me	91	91:9
7	**g**	*t*Bu	H	4-Cl	Me	Me	44	92:8
8	**h**	*t*Bu	H	2,4,6-Me_3	Me	Me	46	> 99:1
9	**i**	*t*Bu	4-MeO	H	Me	Me	82	91:9
10	**j**	*t*Bu	2-MeO, 6-Me	H	Me	Me	50[c]	> 99:1
11	**k**	*t*Bu	2-MeO, 6-Me	4-MeO	Me	Me	75[c]	> 99:1
12	**l**	*t*Bu	2-MeO, 6-Me	2-MeO	Me	Me	59[c]	> 99:1
13	**m**	*t*Bu	2-MeO, 6-Me	4-Cl	Me	Me	17[c]	> 99:1
14	**n**	*t*Bu	2-MeO, 6-Me	H	H	Et	34	97:3
15	**o**	*t*Bu	2-MeO, 6-Me	4-MeO	H	Et	68	> 99:1
16	**p**	*t*Bu	2-MeO, 6-Me	2-MeO	H	Et	51	> 99:1

[a] All β-amino acid esters **7** and **8** were identified from 250 or 400 MHz ^{1}H NMR spectra ($CDCl_3$) and gave correct elemental analyses and/or high-resolution mass spectra. [b] Determined from the crude reaction mixture by HPLC. [c] **7j**: $[\alpha]_D^{22} = -79.9$ ($c = 0.5$, $CHCl_3$); **7k**: $[\alpha]_D^{22} = -98.5$ ($c = 0.5$, $CHCl_3$); **7l**: $[\alpha]_D^{22} = -103.4$ ($c = 0.5$, $CHCl_3$); **7m**: $[\alpha]_D^{22} = -87.9$ ($c = 0.5$, $CHCl_3$).

diastereomeric ratio is higher when the imine nitrogen atom carries an aromatic substituent than in the presence of an alipahtic residue. Thus, **7c**, which is derived from aniline, is obtained with an isomer ratio of 93:7 (Table 1, entry 3), but, if the corresponding imine obtained from benzylamine is employed the two diastereomers are formed in a ratio of only 83:17. Particularly striking is the observation that the stereoselectivity in the Mannich-type reaction increases sharply if either the aromatic group at the imine nitrogen or the carbon atom of the C=N bond carries *ortho* substituents. Thus, if the phenyl ring that stems from the aldehyde is *ortho*- or *para*-substituted, **7** and **8** are formed in ratios of 91:9 to 92:8, respectively (Table 1, entries 4–7). If however two *ortho*-substituents are present, the diastereomer ratio rises to greater than 99:1 (Table 1, entry 8). When the aniline phenyl ring has a *para*-methoxy substituent the two amino acid esters **7i** and **8i** are obtained in a ratio of 91:9 (Table 1, entry 9). However, if the aniline ring contains two *ortho* substituents the Mannich adducts are consistently formed in diastereomerically pure form (Table 1, entries 10–13; the second diastereomer could not be detected by 400 MHz NMR spectroscopy and by HPLC). Several substituted Schiff bases, as well as the imine derived from benzaldehyde itself, gave the desired Mannich adducts with diastereomer ratios greater than 99:1 (Table 1, entries 11–13).

The excellent diastereoselectivity observed in the reactions described above is not restricted to the use of silylketene acetal **5**. If nucleophile **6** is employed instead, the desired β-amino acid derivatives **7** are obtained with nearly complete diastereoselectivity as well (Table 1, entries 14–16). These results demonstrate that by proper choice of the aniline part of the Schiff base the steric course of the Mannich reactions investigated can be steered with complete selectivity.

In another experiment we have additionally employed silylketene acetal **9** in the Mannich-type reaction (Scheme 2).

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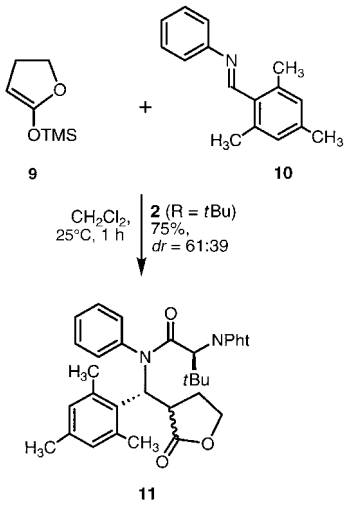


Scheme 2. Asymmetric Mannich reaction of Schiff base **10** with silylketene acetal **9** and *N*-Pht-*t*Leu (**2**; R = *t*Bu) as the chiral auxiliary.

The addition of the carbon nucleophile **9** to the C=N bond once more proceeds exclusively from one face of the iminium intermediate (>99:1). However, the diastereomer ratio is only moderate.

The best results were obtained if the asymmetric Mannich reactions were run without any additional Lewis acid. Thus, if for instance titanium, tin, or boron Lewis acids were added to the reaction mixtures the desired Mannich adducts could not be isolated. Also, lowering the reaction temperature resulted in a reduced rate of reaction, but did not increase the stereoselectivity. The presence of the phthaloyl protecting group appears to be important. Only a low level of stereoselectivity was reached if *Z*-protected proline for instance was used as the chiral auxiliary (*Z* = benzyloxycarbonyl). In addition, *N*,*N*-phthaloylamino acid chlorides are not prone to racemization.[5]

The relative configuration of the major diastereomers **7** was determined by crystal structure analysis of the Mannich adduct **7h**.[7] Since **7h** contains an (*S*)-α-amino acid the configuration of the newly formed stereocenter in the β-amino acid part could be determined unambiguously.

To explain the high stereoselectivity attained through the Mannich reactions detailed above, we assume that the transformations proceed preferentially via transition states **A** (Figure 1). Here the two double bonds of the acyliminium structure are in a coplanar *E-trans* orientation. In this arrangement the stereogenic center of the amino acid part is closer to the imine carbon atom than in the analogous *E-cis* conformation, which explains the marked influence of the steric demand of the amino acid side chain on the stereoselectivity. Furthermore, by analogy to the preferred configuration of α,β-unsaturated amides,[8] the two hydrogen atoms on the imine C=N bond and the amino acid α carbon atom point towards each other. In the corresponding *Z-trans* arrangement a less favorable interaction between the amino acid α hydrogen atom and the aromatic ring on the imine carbon atom would be encountered. The two aromatic rings lie close to each other in **A**, and it may be assumed that in order to minimize unfavorable steric interactions one of the

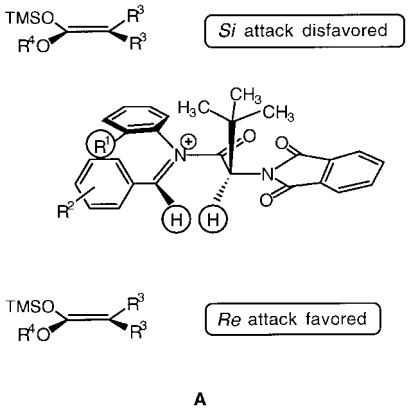
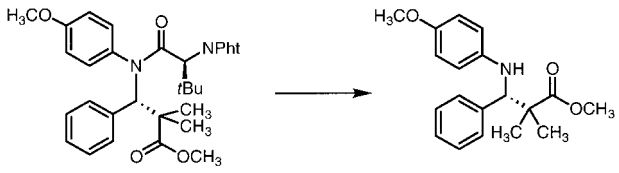


Figure 1. Possible transition state of the Mannich reaction.

two phenyl groups will be tilted away from the other and adopt a conformation in which the aromatic ring is perpendicular to the C=N group. This effect should be particularly pronounced if *ortho* substituents are present on the N-aryl group, which for steric and electronic reasons would preferably point away from the oxygen atom of the carbonyl group.

The chiral auxiliary can readily be removed from the Mannich adducts **7** by a simple two-step sequence. As shown in Scheme 3 for **7i**, first the phthaloyl group was cleaved off by partial reduction with $NaBH_4$ in a 2-propanol/water



Scheme 3. Removal of the chiral auxiliary from the Mannich adduct **7i**. Conditions: 1) $NaBH_4$, *i*PrOH/H_2O 7/1 then aqueous HCl, 80°C, 97%; 2) PhNCS, room temperature, then CF_3COOH/CH_2Cl_2 1/5, heat, 84%.

mixture followed by acidic hydrolysis.[9] The N-deprotected amino acid amide obtained thereby was then subjected to an Edman degradation[10] to give the desired N-arylated β-amino acid ester **12** in high yield. The alkoxy substituted N-aryl group present in the Mannich adducts **7** can be cleaved off by oxidation with, for example, cerium ammonium nitrate.[11] Thus, the phthaloyl group from **7j** was removed by the two-step sequence detailed above. Then the *ortho* methoxy-substituted N-aryl group was cleaved off by treatment with cerium ammonium nitrate to give the desired N-deprotected β-amino acid methyl ester in 52% yield. Its specific rotation ($[\alpha]_D^{22} = +34.7$; $c = 0.21$, 1M HCl) is in very good agreement with literature data $[\alpha]_D^{26} = +34.6$ ($c = 0.17$, 1M HCl),[4c] and proves once more the absolute configuration of the Mannich adducts **7**.

In conclusion the results detailed above demonstrate that the steric course of the Mannich reaction can be directed efficiently by the use of *N*,*N*-phthaloylamino acids. Chiral β-amino acid esters can be obtained by this process with excellent stereoselectivity.

  1433-7851/99/3801-0186 $ 17.50+.50/0

Experimental Section

A solution of *N*-Pht-*tert*-leucine chloride (1.2 mmol) in CH_2Cl_2 (3 mL) was added at 0 °C to a solution of the imine (1 mmol) in CH_2Cl_2 (2 mL). After the mixture was stirred for 30 min at room temperature it was again cooled to 0 °C, and the silylketene acetal (1.5 mmol) added. The reaction mixture was stirred and warmed to room temperature over 72 h, then CH_2Cl_2 (10 mL) was added. The solution was then extracted with a 10% $NaHCO_3$ solution (10 mL) and a saturated NaCl solution (10 mL). The organic layer was dried with Na_2SO_4 and the solvent evaporated in vacuo. The products were isolated from the remaining residue by flash chromatography on silica gel with hexane/ethyl acetate mixtures as eluents. For yields and diastereomer ratios see Table 1.

7k: m.p. 146 °C; $[\alpha]_D^{22} = -98.5$ ($c = 0.5$ in $CHCl_3$); ^{1}H nmr (500 MHz, $CDCl_3$): $\delta = 0.65$ (s, 3H; CH_3, anisidine), 1.11 (s, 3H; *t*Bu), 1.16 (s, 3H; CH_3), 1.54 (s, 3H; CH_3), 3.60 (s, 3H; OCH_3), 3.67 (s, 3H; OCH_3), 3.95 (s, 3H; OCH_3), 4.34 (s, 1H; αH, *t*Leu), 6.08 (d, $^3J = 8$ Hz, 1H; *o*H, aryl), 6.44 (s, 1H; βH), 6.50 (d, $^3J = 8$ Hz, 2H; *m*H, aryl), 6.71 – 6.75 (br s, 2H; 3- and 5-H, anisidine), 6.86 (d, $^3J = 8$ Hz, 1H; *o*H, aryl), 7.08 (dd, $^3J_1 = {}^3J_2 = 8$ Hz, 1H; 4-H, anisidine), 7.51 (d, $^3J = 7$ Hz, 1H; *o*H, Pht), 7.61 (ddd, $^3J_1 = {}^3J_2 = 7$ Hz, $^4J = 1$ Hz, 1H, *m*H, Pht), 7.65 (ddd, $^3J_1 = {}^3J_2 = 7$ Hz, $^4J = 1$ Hz, 1H; *m*H, Pht), 7.74 (d, $^3J = 7$ Hz, 1H; *o*H, Pht); ^{13}C nmr (125.8 MHz, $CDCl_3$): $\delta = 17.57$ (($CH_3)_2$C), 21.34 (($CH_3)_2$C), 24.40 (CH_3, anisidine), 27.86 (3C, *t*Bu), 37.32 (($CH_3)_2$*C*), 50.14 (*t*Bu), 51.69 (OCH_3), 54.69 (OCH_3), 54.92 (OCH_3), 58.41 (β-CH), 65.52 (αCH-*t*Leu), 109.50 (3C, anisidine), 112.27 (*m*-C, aryl), 122.36 (5-C, anisidine), 122.71 (*o*-C, Pht), 122.95 (*o*-C, Pht), 127.11 (1-C, anisidine), 128.29 (6-C, anisidine), 129.12 (*o*-C, aryl), 130.68 (1-C, aryl), 132.29 (C, Pht), 133.53 (*m*-C, Pht), 133.85 (4-C, anisidine), 141.07 (C, Pht), 155.87 (*p*-C, aryl), 158.74 (4-C, anisidine), 166.27 (C(O), *t*Leu), 167.47 (2C, C(O), Pht), 177.21 (CO_2CH_3); HR-MS: calcd for $C_{35}H_{40}N_2O_7$ [M^+] 600.2836; found: 600.2823; elemental analysis calcd for $C_{35}H_{40}N_2O_7$: C 69.98, H 6.71, N 4.66; found: C 69.86, H 6.72, N 4.83.

Received: June 5, 1998
Supplemented version: September 30, 1998 [Z 11953 IE]
German version: *Angew. Chem.* **1999**, *111*, 166 – 169

Keywords: amino acids · asymmetric synthesis · chiral auxiliaries · Mannich reaction

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Tetrakis(2,4,6-triisopropylphenyl)diplumbene: A Molecule with a Lead – Lead Double Bond**

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Dedicated to Professor Helmut Werner on the occasion of his 65th birthday

Disilenes, digermenes, and distannenes—compounds with Si–Si, Ge–Ge, and Sn–Sn double bonds—are now well-established molecules, and their properties have been summarized in several review articles.[1, 2] They are usually prepared by the primary generation of the carbene analogues R_2E: (E = Si, Ge, Sn) and subsequent dimerization. Diplumbenes, molecules with a lead – lead double bond, were unknown until now. Furthermore, structurally characterized dialkyl-[3, 4] and diarylplumbylenes (-plumbanediyls)[5, 6] were reported for the first time in the past few years. The latter particles with electron sextets exist both in solution and in the crystal as monomers without noticeable Pb–Pb interactions.

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[**] Compounds of Germanium, Tin, and Lead. Part 28. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. Part 27: M. Weidenbruch, U. Grobecker, W. Saak, E.-M. Peters, K. Peters, *Organometallics* **1998**, *17*, 5206.

  1433-7851/99/3801-0187 $ 17.50+.50/0