Erratum for: Titanium-Mediated Addition of Silyl Dienol Ethers to Electrophilic Glycine: 4-Ketopipelic Acid Hydrochloride

Clarisse Mühlemann, Peter Hartmann, and Jean-Pierre Obrecht

Dr.R.Maag AG (CRD), from 1990 Ciba-Geigy Plant Protection Division (Disease Control), Ueberlandstrasse 138, CH-8600 Duebendorf, Switzerland.

Checked by Eugene Ho and David L. Coffen
Rechecked by Yasuhiro Shimamoto, Heemal Dhanjee and John L. Wood

Procedure

A. 2-Bromo-N-Boc-glycine tert-butyl ester. A 500 mL round-bottomed flask equipped with an egg-shaped, teflon-coated magnetic stir bar (3.0 cm x 1.5 cm) is capped with a rubber septum. The flask is placed under nitrogen by way of a needle through the rubber septum (Note 1). The septum is removed temporarily, N-Boc-glycine tert-butyl ester (10.0 g, 43.2 mmol,
1.0 equiv) (Note 2) and N-bromosuccinimide (8.10 g, 45.5 mmol, 1.05 equiv) (Note 3) are added. The flask is placed under vacuum and backfilled with nitrogen three times after which chlorobenzene (175 mL, 0.25 M) (Note 4) is added. The flask is then cooled in an ice water bath, and irradiated with a 300 W tungsten lamp for 1 h (Note 5) (Figure 1) during which the colorless solution becomes a dark red solution. The suspension is filtered using a fritted filter funnel (4.5 cm diameter, Fine) and chlorobenzene is removed under reduced pressure using a rotary evaporator (50 mmHg, 40 °C). The residue is further dried under high vacuum (1.0 mmHg, 25 °C) for 2 h. The yellow crude oil is used in the next step without further purification (Note 6).

**Figure 1. Reaction Set-up for Step A.**

**B. tert-Butyl [1-(tert-butoxycarbonyl)-3-oxo-4-pentenyl]carbamate.** The crude bromination product from the previous step is taken up in dry tetrahydrofuran (120 mL) (Note 7) and transferred to a 500 mL 3-necked round-bottomed flask equipped with an egg-shaped, teflon-coated magnetic stir bar (3.0 cm x 1.5 cm), a rubber septum with thermocouple temperature probe (Neck 1), a 100-mL dropping funnel capped with a rubber septum (Neck 2), and a nitrogen inlet (Neck 3) (Figure 2). The solution is cooled to –78 °C in a dry ice-acetone bath and a solution of dichlorodiethoxytitanium [TiCl₂(OEt)₂] (21.0 g, 100 mmol, 2.3 equiv) in THF (40 mL, 2.5 M) (Note 8) is
added slowly to ensure the internal temperature does not exceed –72 °C. When the addition is complete, the reaction mixture is stirred for 10 min at which point a solution of 2-trimethylsiloxybutadiene (12.0 g, 85 mmol, 2.0 equiv) (Note 9) in THF (50 mL, 1.7 M) is added dropwise, resulting in a slight increase in temperature (to –72 °C). The reaction mixture is allowed to warm to room temperature. After 12 h, the mixture is poured into 350 mL of ice-cooled, saturated sodium bicarbonate solution and is filtered through a pad of Celite (60 g) using a fritted filter funnel (10 cm diameter, Fine). The celite is washed with diethyl ether (2 x 100 mL). The filtrate is transferred to a 1 L separatory funnel. The layers are separated, and the aqueous phase is extracted with diethyl ether (2 x 100 mL). The combined organic layers are washed with brine (1 x 100 mL), dried over anhydrous sodium sulfate (Na₂SO₄), filtered through a cotton plug and collected in a 1-L round-bottomed flask. The Na₂SO₄ is rinsed with diethyl ether (2 x 20 mL). The solvent is removed under reduced pressure by rotary evaporation (50 mmHg, 30 °C). The dark crude oil is purified by column chromatography. A fritted chromatography column (3.0 cm diameter) is dry-packed with silica gel (20 cm height, 50 g) (Note 10) and then wetted with hexanes under air pressure. The crude oil is loaded directly onto the column and eluted with 1 L of 10:1 hexane/ethyl acetate. The eluent is collected in 25 mL fractions and monitored by TLC (Product Rₜ = 0.11, hexane/ethyl acetate: 10/1) (Notes 6 and 11). The fractions are combined in a 1-L round-bottomed flask and concentrated under reduced pressure by rotary evaporation (50 mmHg, 30 °C) to give tert-butyl [1-(tert-butoxycarbonyl)-3-oxo-4-pentenyl] carbamate as a yellowish oil (2.82 g, 22%) (Note 12).

Figure 2. Reaction Set-up for Step B
C. 1-Carboxy-5-chloro-3-oxopentan-1-aminium chloride. In a 500 mL, one-necked round-bottomed flask, tert-butyl [1-(tert-butoxycarbonyl)-3-oxo-4-pentenyl] carbamate (8.72 g, 29.1 mmol, 1.0 equiv) is dissolved in an ice-cooled, saturated solution of hydrogen chloride in diethyl ether (280 mL) (Note 14). The solution is kept, without stirring, at room temperature overnight. The solvent is removed with a pipette and the solid sequentially washed with diethyl ether (4 x 100 mL) (Note 13). The resulting solid is dried under reduced pressure (1.0 mmHg, 25 °C) to afford 1-carboxy-5-chloro-3-oxopentan-1-aminium chloride as a pale cream solid (5.56 g, 88%) (Notes 15 and 16).

Notes

1. Unless otherwise noted, all glassware and stir bars were flame dried under vacuum, cooled to room temperature under vacuum, and placed under nitrogen atmosphere.

2. N-Boc-glycine tert-butyl ester was prepared as follows: A 1 L one-necked round-bottomed flask was equipped with an egg shaped stir bar (3.0 cm x 1.5 cm) and capped with a rubber septum. Boc-Gly-OH (99%, purchased from Oakwood Chemical and used as received) (30.2 g, 171 mmol, 1.0 equiv) and DCM (600 mL, 0.29 M) were added. The solution was cooled in ice-water bath, and then tBuOH (15.3 g, 202 mmol, 1.2 equiv), DMAP (1.5 g 12 mmol, 0.07 equiv) and DCC (41.3 g, 200 mmol, 1.2 equiv) were added. The reaction mixture was stirred for 12 h, and the precipitate was filtered using a fritted filter funnel (4.5 cm in diameter, Fine). The filtrate was concentrated under reduced pressure by rotary evaporation (50 mmHg, 30 °C water bath), and the residue was purified by flash column chromatography on silica gel (8.0 cm diameter, 20 cm height of silica gel (400 g)) (Note 10). Hexanes/ethyl acetate: 10/1 (100 mL) and hexanes/ethyl acetate: 5/1 (2000 mL) were used as eluents, which were collected in 50 mL fractions (Note 11). The desired product (R = 0.40, hexane/ethyl acetate: 5/1) containing minor impurities was obtained (33 g). The material was recrystallized twice from hexanes. Hexanes (100 mL) was added and heated to 60 °C so as to dissolve all the solids. The solution was left to cool slowly to room temperature and subsequently placed in a –23 °C freezer for
approximately 12 h. The crystals were then collected on a Kiriyama filter. The recrystallization was repeated a second time to provide N-Boc-glycine tert-butyl ester (16.6 g, 71.8 mmol, 41.9% yield)

3. N-Bromosuccinimide was purchased from Sigma Aldrich, recrystallized from water, and dried in a vacuum desiccator (1.0 mmHg, 25 °C).

4. Chlorobenzene was purchased from Acros Organics and used without further purification. The submitters and previous checkers used CCl₄. Difficulties in obtaining CCl₄ led the current checkers to make this solvent change.

5. The water bath was coated with aluminum foil. Foil was wrapped around the entire reaction assembly in order to increase the efficiency of the irradiation. The checkers used a 300W tungsten lamp while the submitters used a 150W tungsten lamp.

6. TLC (ethyl acetate/hexane 1:3; visualized with vanillin/concd. H₂SO₄/heat) (Note 10) reveals complete consumption of the starting material (starting material Rₜ = 0.47) and only small amounts of impurities are observed by ¹H NMR analysis. The crude product is stable for several weeks at −20 °C under argon.

7. Non-stabilized THF was purchased from Fisher Scientific and passed through two packed columns of neutral alumina in a solvent purification system manufactured by SG Water U.S.A., LLC.

8. The equivalents of reagents used in this reaction are based on the amount of starting material used in step A of the reaction sequence. Tetraethyl orthotitanate, (11.5 g, 50 mmol) was purchased from Sigma-Aldrich and distilled at 110–115 °C at 0.1 mmHg. The distilled material is dissolved in dry THF (40 mL) (Note 7). Titanium chloride (TiCl₄) (9.5 g, 50 mmol) was purchased from Sigma-Aldrich and distilled at 136 °C under atmospheric pressure. The titanium tetrachloride was added dropwise to the solution of tetraethyl orthotitanate while cooling in an acetone/dry ice bath.

9. Trimethylsiloxybutadiene was purchased from Oakwood Chemical, and employed without further purification.

10. Silica gel SilicaFlash® F60 (40-63 µ / 230-500 mesh) was purchased from Silicycle. Glass-backed extra hard layer TLC plates, 60 Å (250 µm thickness) were also purchased from Silicycle containing F-254 indicator.
11. Ethyl acetate and hexanes (all ACS Grade) used in chromatography were purchased from Fisher Scientific and used as received.

12. The submitters obtained a 33–36% yield over this two-step sequence, and the checkers note that the change in solvent from CCl₄ to chlorobenzene and a change in the lamp from 150 W to 300 W could account for this difference in yield. The physical properties are as follows: ¹H NMR (CDCl₃) δ: 1.42 (s, 18 H), 3.07 (dd, 1 H, J = 4.8, 17.6 Hz), 3.28 (dd, 1 H, J = 4.8, 17.6 Hz), 4.44 (m, 1 H), 5.47 (d, 1 H, J = 8.0 Hz, N-H), 5.90 (dd, 1 H, J = 1.2, 10.4 Hz), 6.24 (dd, 1 H, J = 1.2, 17.6 Hz), 6.33 (dd, 1 H, J = 10.4, 18.0 Hz); ¹³C NMR (CDCl₃) δ: 27.8, 28.3, 41.5, 50.1, 82.1, 129.3, 136.2, 155.6, 170.2, 198.3; IR (ATR) cm⁻¹: 3370, 2980, 2930, 1710, 1620, 1490. HRMS (+ESI) calcd for C₁₅H₂₂NO₅ (M+Na) 322.1630. Found 322.1631.

13. This compound is very hygroscopic.

14. Hydrogen chloride in diethyl ether was prepared by bubbling hydrogen chloride into diethyl ether for 2 h. Hydrogen chloride was generated from treatment of NaCl with H₂SO₄.

15. The physical properties are as follows: ¹H NMR (CD₂OD) δ: 3.05 (dt, 2 H, J = 1.2, 6.4 Hz), 3.20 (dd, 1 H, J = 6.8, 18.8 Hz), 3.29 (dd, 1 H, J = 4.0, 19.6 Hz), 3.79 (t, 2 H, J = 6.4 Hz), 4.30 (dd, 1 H, J = 4.0, 6.8 Hz); ¹H NMR (400 MHz, D₂O) δ: 3.11 (t, 2H, J = 6.0 Hz), 3.32–3.34 (m, 2H), 3.81 (t, 2H, J = 6.0 Hz), 4.27 (dd, 1H, J = 4.4, 6.0 Hz); ¹³C NMR (100 MHz, CD₂OD) δ: 28.0, 38.7, 42.9, 45.7, 48.4, 170.9, 205.6; ¹³C NMR (100 MHz, D₂O) δ: 37.9, 41.7, 44.1, 48.5, 171.4, 207.8; IR (ATR) cm⁻¹: 3300–2300 broad, 1720, 1580, 1400. HRMS (+ESI) calcd for C₁₅H₂₃ClNO₅ (M-Cl) 180.0422. Found 180.0424. mp = 116 – 118 °C (decomp).

16. In an effort to confirm the structure, the checkers employed the illustrated procedure to convert 1-carboxy-5-chloro-3-oxopentan-1-aminium chloride to 2-tert-butoxy carbonylamino-6-chloro-4-hexanolide, a compound which had been stereoselectively prepared previously by Hesse.²
In a 100 mL one-necked round-bottomed flask equipped with a 2.0 cm x 0.5 cm rod shaped stir bar, 1-carboxy-5-chloro-3-oxopentan-1-ammonium chloride (500 mg, 2.3 mmol, 1.0 equiv) is dissolved in MeOH (10 mL, 0.23 M) and cooled in an ice-water bath. NaBH₄ (130 mg, 3.5 mmol, 1.5 equiv) is added and the reaction stirred for 2 h. The solvent is removed under reduced pressure by rotary evaporation (50 mmHg, 30 °C water bath). The crude alcohol is then dissolved in 1 M aq. HCl (20 mL) and stirred for 2 h after which the solvent is removed under reduced pressure (1.0 mmHg, 25 °C water bath). The lactonized ammonium salt is subsequently dissolved in dioxane/H₂O (1/1) (50 mL), and treated with NaHCO₃ (1.9 g, 23 mmol, 10 equiv) followed by Boc₂O (610 mg, 2.8 mmol, 1.2 equiv). The reaction mixture is stirred for 12 h, after which time the reaction mixture is extracted with ethyl acetate (3 x 30 mL). The combined organic layers are washed with brine (1 x 30 mL), dried over Na₂SO₄, filtered, and concentrated under reduced pressure by rotary evaporation (50 mmHg, 30 °C water bath). The residue is purified by flash column chromatography on silica gel. Hexanes/ethyl acetate:3/1 (500 mL) is used as the eluent and collected in 10 mL fractions. The fractions were monitored by TLC (Rf = 0.18, hexane/ethyl acetate: 3/1). The first fractions were concentrated to give 12.3 mg of the cis-isomer (2.0% over 3 steps). The last fractions were concentrated under reduced pressure to give 10.3 mg of the trans-isomer (1.7% over 3 steps), and the middle fractions were concentrated under reduced pressure to provide 182 mg of a 47:53 cis:trans (30% over 3 steps). In all cases was the 2-tert-butyloxycarbonylamino-6-chloro-4-hexanolide obtained as a white solid. cis: ¹H NMR (CDCl₃) δ: 1.45 (s, 9 H), 1.88 (q, 1 H, J = 12.0 Hz), 2.05–2.14 (m, 1 H), 2.17–2.26 (m, 1 H), 2.84–2.93 (m, 1 H), 3.66–3.72 (m, 2 H), 4.35–4.47 (m, 1 H), 4.62–4.69 (m, 1 H), 5.09 (bs, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ: 28.2, 36.4, 38.0, 40.3,
51.4, 74.6, 80.7, 155.3, 174.3; IR (ATR) cm$^{-1}$: 3420, 2980, 2930, 1770, 1700, 1510. *trans:* $^1$H NMR (CDCl$_3$) δ: 1.45 (s, 9 H), 1.97–2.07 (m, 1 H), 2.12–2.20 (m, 1 H), 2.34–2.53 (m, 2 H), 3.66 (dd, 2H, $J$ = 5.2, 7.6 Hz), 4.32–4.45 (m, 1 H), 4.84–4.93 (m, 1 H), 5.09 (bs, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 28.2, 34.3, 38.1, 40.3, 49.2, 74.3, 80.9, 155.4, 174.7; IR (ATR) cm$^{-1}$: 3380, 2980, 2930, 1780, 1670, 1520, HRMS (+ESI) calcld for C$_{11}$H$_{18}$ClNO$_4$ (M+Na) 286.0822. Found 286.0819. Melting Point: 121.4–123.1 °C.

To unambiguously confirm the identity of the lactone product, the checkers prepared single crystals suitable for X-Ray crystallographic analysis using the *trans*-isomer (Figure 3). Single crystals are grown from a DCM solution of the *trans*-isomer by vapor diffusion into hexanes. Accordingly, 10 mg of *trans*-2-tert-butyloxycarbonylamino-6-chloro-4-hexanolide are placed in a 1.5 dram vial and dissolved in a minimal amount of DCM (ca. 0.5 mL). This vial is placed into a larger 50 mL jar containing a volume of hexanes such that the meniscus is slightly above that of the DCM in the inner vial. The larger vial is sealed and let stand at room temperature to produce colorless cube crystals (ca. 6 h). Single crystal X-ray diffraction data were collected on a Bruker Apex II-CCD detector using Mo-K$_\alpha$ radiation (λ= 0.71073 Å). Crystals are removed from the mother liquor and coated in an inert perfluoro-polyether oil, mounted on micromounts then placed in a cold stream of N$_2$. Structures were solved and refined using SHELXTL (Table 1). These data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary

![Figure 1. The molecular structure of *trans*-2-tert-butyloxycarbonylamino-6-chloro-4-hexanolide from the crystal structure.](image-url)
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Discussion

In February of 2015 Professor RFW Jackson from the University of Sheffield brought to the attention of the *Organic Syntheses* editorial board his
suspicions that a structural misassignment had been made for the final product reported in a 1993 Organic Syntheses procedure that had been submitted by Jean-Pierre Obrecht and checked by David Coffen. In response to considerable information provided by Professor Jackson and his suggestion that Step C in this procedure converts 1 to 3 rather than the reported cyclized product 2, the editorial board determined that rechecking of the procedure was in order. The procedure illustrated above reflects this rechecking effort. In the course of these recent investigations every effort was made to reproduce the original report, but due to the difficulty in obtaining carbon tetrachloride a solvent change was necessitated in step A. Although this minor change impacts yield, the physical properties and spectral data obtained for 1 were consistent with the 1993 report. Subjecting this material to conditions identical to those reported in step C of the 1993 Organic Syntheses procedure confirmed Professor Jackson’s suggestion that this reaction does indeed furnish 3 rather than 2 (Scheme 1).

![Scheme 1: Discrepancy Discovered by R.F.W. Jackson and M.L. Chilton](image)

Although it is noteworthy that spectral data obtained for the product derived from 1 differs from that reported for 2 in papers published by Burger in 1995 and 1996, positive proof for the structural reassignment was sought via elemental composition data. Mass spectrometry was indicative of structure 3 but efforts to obtain an acceptable elemental analysis furnished results outside the acceptable ± 0.4% window, although the data obtained from multiple EA attempts were all more consistent with structure 3 than for 2. Given the inability to obtain satisfactory EA data the checkers turned to chemical correlation as a means of providing compelling evidence.
for structure 3 and thus attempted to convert 3 to lactones (±)-6 and (±)-7, the former of which had been previously prepared in enantiopure form via an unrelated route by Hesse (Scheme 2).² Although, spectral data obtained by the checkers for (±)-6 was similar to that reported for (+)-6 by Hesse, there were clear discrepancies in both the ¹H and ¹³C NMR data. Thus, the checkers turned to X-ray crystallography in order to confirm the structure. To this end trans-lactone (±)-7 was found to furnish crystals suitable for X-ray analysis and the derived structure provided convincing proof that the compound 3 is precursor to 7 and thus does indeed arise upon treatment of 1 with HCl in Et₂O.

Scheme 3: Chemical correlation to reported synthesis of (+)-6 by Hesse.
References

5. R.F.W. Jackson reported to the checkers that they had experienced similar difficulties in obtaining EA data and also observed greater consistency of their data with structure 3.

Appendix

**Chemical Abstracts Nomenclature (Registry Number)**

- Glycine (513-29-1)
- *N*-Bromosuccinimide (128-08-5)
- Titanium chloride (7550-45-0)
- Triethylamine (121-44-8)
- 2-Trimethylsiloxynbutadiene (38053-91-7)
- Di-*tert*-butyl dicarbonate (24424-99-5)
- 4-Ketopipeolic acid hydrochloride,
- Pipecolic acid, 4-oxo-, hydrochloride (99979-55-2)
- 2-Bromo-*N*-Boc-glycine *tert*-butyl ester,
- *N*-Boc-2-Bromoglycine *tert*-butyl ester
- *N*-Boc-glycine *tert*-butyl ester,
- Boc-Glycine *tert*-butyl ester (111652-20-1)
- *tert*-Butyl [1-(*tert*-butoxycarbonyl)-3-oxo-4-pentenyl]carbamate (117833-62-2)
- Dichlorodiethoxytitanium (3582-00-1)
- Glycine *tert*-butyl ester hydrochloride (27532-96-3)
- Tetraethyl orthotitanate (3087-36-3)
- *N*-Boc-glycine (4530-20-5)
Yasuhiro Shimamoto obtained his undergraduate degree from Kyoto University in 2009 in Engineering. He subsequently obtained his Ph.D. from Professor Masahiro Murakami in Engineering in 2014. He is currently a Post-Doctoral scholar in the laboratory of Professor John L. Wood at Baylor University.

Heemal Dhanjee obtained his B.A. in Mathematics and Molecular and Cell Biology at the University of California, Berkeley in 2007. He subsequently moved to California State University, Northridge and performed research in organic synthesis under the supervision of Professor Thomas Minehan. He is currently pursuing graduate research at Baylor University under the guidance of Professor John L. Wood.
OrgSynP2-CD3OD.11.fid
Crystal structure of...

*trans*-2-*tert*-Butyloxycarbonylamino-6-chloro-4-hexanolate

**Table 1.**

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*Note: $R_{1}(I>2\sigma(I)) = \frac{\sum |F_o|-|F_c|}{\sum |F_o|}$; $wR_2(F^2) = \left[\frac{w(F_o^2-F_c^2)^2}{\sum w(F_o^2)}\right]^{1/2}$; $S$(all data) = $\left[\frac{\sum w(F_o^2-F_c^2)^2}{(n-p)}\right]^{1/2}$ (n = no. of data; p = no. of parameters varied; $w = \frac{1}{(F_o^2+F_c^2)/3}$ and $a$ and $b$ are constants suggested by the refinement program.*