Efficient Synthesis of 4,5-Disubstituted-3-toluenesulfonyl Glutarimides. Application to the Formal Synthesis of Mappicine Ketone

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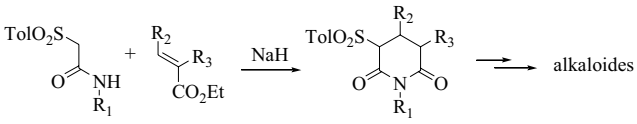
Various 4,5-disubstituted-3-sulfonyl glutarimides **3** were synthesized from α-sulfonyl acetamide **1** and ethyl α,β-disubstituted acrylate esters **2** via stepwise facile [3+3] annulation in moderate yield. The synthesis of pyridin-2-one **9**, a key intermediate for mappicine ketone (**4**) synthesis, was also reported.

Keywords: Ethyl α,β-disubstituted acrylate esters; [3+3] Annulation; Mappicine ketone.

INTRODUCTION

Glutarimides possess various biological activities.[1] Therefore, the preparation of these cyclic imides has attracted considerable attention from organic chemists.[2] Previously, we reported an efficient route to N-benzyl-3-sulfonyl-4 or 5-substituted glutarimides **3** via stepwise [3+3] cycloaddition of N-benzyl α-sulfonylacetamide **1** with α,β-unsaturated esters **2**. We then further converted **3** to various six-membered nitrogen containing heterocycles and alkaloids[3] (Shceme I). In this paper, we extended the results to the synthesis of N-benzyl-4,5-disubstituted-3-sulfonyl glutarimides. Synthetic study toward mappicine ketone (**4**)[4] (Fig. 1) is also reported.

Shceme I



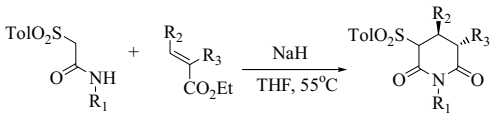
1 **2** **3**

RESULTS AND DISCUSSION

Synthesis of 4,5-dimethyl-3-toluenesulfonyl glutarimide 3a

We first investigated the reaction of **1** with ethyl tiglate. A mixture of N-benzyl α-sulfonylacetamide **1** and 3 equiv of sodium hydride in THF was allowed to react at room temperature for 10 min, then 4 equiv of ethyl tiglate was added in one portion and the solution was further stirred at 55 °C for 12 hours. After general workup, the desired glutarimide **3a** was isolated as a mixture in 71% yield. Encouraged by this result, various ethyl α,β-disubstituted acrylate esters **2** were examined. The corresponding trisubstituted glutarimides **3** were obtained in moderate yield.

Table 1. Reaction of α-toluenesulfonylacetamide **1** and ethyl α,β-disubstituted acrylate esters **2**

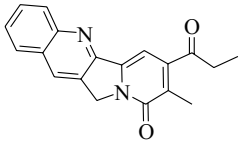


1 **2** **3**

Entry	R_1	R_2	R_3	Product[5] (yield %)
1	—Bn	$-CH_3$	$-CH_3$	3a (71)[a]
2	—Bn	$-CH(OCH_3)_2$	$-CH_3$	3b (40)[b]
3	—Bn	$-CH(OCH_3)_2$	$-CH_2CH_3$	3c (43)[b]
4	—PMB	$-CH_2OBn$	$-CH_3$	3d (81)[a]

a. a mixture of two stereoisomers
b. one stereoisomer

The scope of the reaction appears to be limited to dialkyl α,β-disubstituted acrylic acid ethyl esters. It is worth noting that entries 2 and 3 gave low yields. In the reactions of β-aryl-α-alkyl or β,β-disubstituted acrylic acid



Mappicine ketone (**4**)

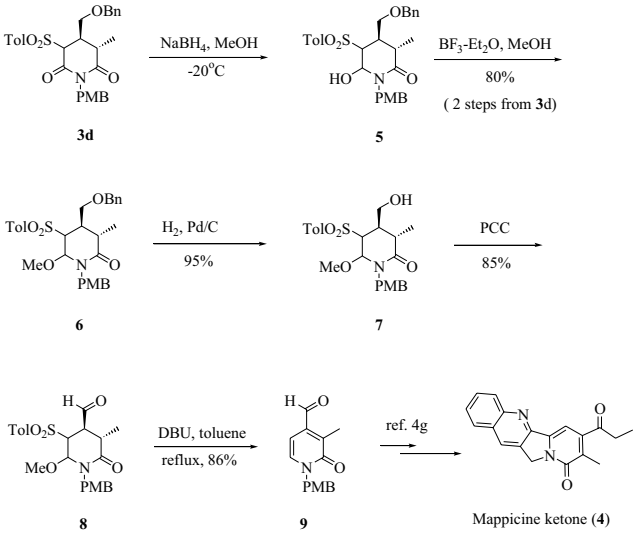
Fig. 1

ethyl esters, no desired glutarimides were obtained. The presence of large substituent(s) at the β-position in ester might account for the results.

Preparation of pyridin-2-one 9, a key intermediate for the synthesis of mappicine ketone (4)

To demonstrate the synthetic utility of these results, the synthesis of pyridin-2-one **9**, the key intermediate for mappicine ketone synthesis,[4a] was investigated. As depicted in Scheme II, regioselective reduction of **3d** with excess sodium borohydride in methanol-tetrahydrofuran (1:2) at -20 °C furnished hydroxy lactam **5**. Without purification, lactam **5** was treated with methanol in the presence of BF_3-Et_2O to afford methoxy lactam **6** in 80% yield (two steps from **3d**). Removal of the benzyl protection in **6** with hydrogen gas at 1 atm in the presence of palladium catalyst obtained alcohol **7** in 95% yield. Oxidation of the primary alcohol in **7** with PCC furnished the corresponding aldehyde **8** in 85% yield. Base promoted double elimination of **8** with DBU afforded pyridin-2-one **9**. Pyridin-2-one **9** has been converted to mappicine ketone (**4**).[4a]

Scheme II



CONCLUSION

In summary, we have successfully generated 4,5-disubstituted 3-toluenesulfonyl glutarimides via a one pot procedure. This methodology has proved to be applicable for the synthesis of mappicine ketone (**4**). Further application of these results in the synthesis of camptothecin and other related alkaloids is currently underway in our laboratory.

EXPERIMENTAL

General

Before use, THF was distilled from a deep blue solution resulting from sodium and benzophenone under nitrogen. All reagents and solvents were obtained from commercial sources and used without further purification. Thin layer chromatography (TLC) analysis was performed with precoated silica gel (60 f254 plates) and column chromatography was carried out on silica (70~230 mesh). All reactions were performed under an atmosphere of nitrogen in dried (except those concerned with aqueous solutions) spherical flasks and stirred with magnetic bars. Organic layers were dried with anhydrous magnesium sulfate before concentration in vacuo.

General procedure to 4,5-disubstituted-3-toluenesulfonyl glutarimides (3a)-(3d)

A solution of α-toluenesulfonyl acetamide **1** (1.0 mmole) in THF (20 mL) was added to a rapidly stirred suspension of sodium hydride (60% dispersion in mineral oil, 3.0 mmole). After the reaction mixture was stirred at room temperature for 10 minutes, 4.0 mmole of α,β-unsaturated esters **2** was then added to the suspension mixture. The mixture was stirred at 55 °C for 12 h, quenched with water (5 mL) and extracted with AcOEt (3 × 20 mL). The organic layers were washed with brine, dried with anhydrous $MgSO_4$, filtered and evaporated. The residue was purified by column chromatography on silica gel (elution with hexane/ethyl acetate = 4:1) to give 4,5-disubstituted-3-toluenesulfonyl glutarimides **3**.

For **3a**: 71% Yield; colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ) 7.61-7.46 (d, J = 8.5 Hz, 2H), 7.36-7.20 (m, 7H), 5.05-4.82 (dd, J = 14 Hz, 14 Hz, 2H), 3.94-3.92 (m, 1H), 3.63-3.58 (m, 1H), 3.15-3.10 (m, 1H), 2.76-2.69 (m, 1H), 2.45-2.43 (s, 3H), 1.50 (d, J = 7 Hz, 3H), 1.35 (d, J = 6.5 Hz, 3H). Ratio = 1:1.5 base one δ) 7.59: δ) 7.46. LRMS *m/z* (ESI, M^++1, 2.5e +0.6): 386. HRMS (ESI) calcd for $C_{21}H_{24}NO_4S$ (M^+ +1) 386.1426, found 386.1424.

For **3b**: 40% Yield; pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ) 7.58 (d, J = 8.5 Hz, 2H), 7.33-7.22 (m, 7H), 4.99 (d, J = 14 Hz, 1H), 4.89 (d, J = 14 Hz, 1H), 4.37 (s, 1H), 4.21 (d, J = 3.5 Hz, 1H), 3.38 (s, 3H), 3.06 (d, J = 3.5 Hz, 1H), 2.81 (q, J = 8 Hz, 1H), 2.44 (s, 3H), 1.66 (d, J = 8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ) 174.24, 164.63, 145.31, 136.61, 135.38, 129.72 (2C), 128.92 (2C), 128.64 (2C), 128.11 (2C), 127.18, 107.29, 65.14, 59.34,

55.93, 43.95, 37.68, 35.94, 21.72, 18.92. IR ($CHCl_3$, cm^{-1}): 2401, 2305, 1676, 1552. LRMS *m/z* (EI, 30 eV): 445 (1.7%), 290 (58.15%), 91 (94.02%), 75 (100%). HRMS (FAB) calcd for $C_{23}H_{27}NO_6S$ (M^++1) 446.1644, found 446.1637.

For **3c**: 43% Yield; pale yellow oil; ^1H NMR (500 MHz, $CDCl_3$): δ) 7.67 (d, *J* = 9 Hz, 2H), 7.34-7.20 (m, 7H), 4.98 (d, *J* = 14.5 Hz, 1H), 4.91 (d, *J* = 14.5 Hz, 1H), 4.43 (s, 1H), 4.18 (d, *J* = 3 Hz, 1H), 3.39 (s, 3H), 3.23 (d, *J* = 1.5 Hz, 1H), 3.18 (s, 3H), 2.58 (t, *J* = 3 Hz, 1H), 2.44 (s, 3H), 2.19-2.01 (m, 2H), 1.11 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ) 173.56, 164.63, 145.17, 136.64, 136.12, 129.69 (2C), 128.89 (2C), 128.42 (2C), 128.06 (2C), 127.08, 107.67, 64.62, 56.43, 55.86, 43.70, 43.36, 34.88, 25.61, 21.68, 12.14. IR ($CHCl_3$, cm^{-1}): 1672. LRMS *m/z* (FAB): 460 (1.07%), 272 (54.3%), 91 (100%), 75 (90.73%). HRMS (FAB) calcd for $C_{24}H_{30}NO_6S$ (M^++1) 460.1794, found 460.1787.

For **3d**: 81% Yield; pale yellow oil; ^1H NMR (500 MHz, $CDCl_3$): δ) 7.45 (d, *J* = 8.5 Hz, 2H), 7.36-7.24 (m, 7H), 7.18 (d, *J* = 7.5 Hz, 2H), 6.80 (d, *J* = 8.5 Hz, 2H), 4.90-4.74 (m, 2H), 4.41 (d, *J* = 6 Hz, 2H), 4.22 (d, *J* = 3.5 Hz, 1H), 3.77 (s, 3H), 3.68-3.53 (m, 2H), 2.87-2.83 (m, 1H), 2.73-2.68 (m, 1H), 2.45 (s, 3H), 1.52 (d, *J* = 7.5 Hz, 3H). LRMS *m/z* (ESI, M^++1, 2.5e+0.6): 522. HRMS (ESI) calcd for $C_{29}H_{32}NO_6S$ (M^++1) 522.1950, found 522.1953.

4-Benzyloxymethyl-6-methoxy-1-(4-methoxybenzyl)-3-methyl-5-(toluene-4-sulfonyl)-piperidine-2-one (6)

A suspension of sodium borohydride (8.0 mmole) and glutarimides **1** (1.5 mmole) in THF (30 mL) and methanol (15 mL) was stirred for 2 h at -20 °C. After saturated aqueous sodium bicarbonate was added to destroy the excess reduction agent at this temperature, organic solvents were removed under reduced pressure. The residue was extracted with dichloromethane, and the combined organic extracts were washed with brine, dried, filtered, and concentrated to afford **5**. Without further purification, boron trifloride diethyl etherate (0.5 mL) was added to a solution of crude 5 in MeOH (20 mL) at 0 °C and stirred at this temperature for 30 min. The reaction mixture was quenched with saturated aqueous sodium bicarbonate. The layers were separated, and the aqueous layer was extracted with dichloromethane. The combined organic layers were washed with brine, dried, filtered, and concentrated. The residue was purified by column chromatography on silica gel (elution with hexane/ethyl acetate 2:1) to give methoxy lactam **6**, pale yellow oil. ^1H NMR (500 MHz, $CDCl_3$): δ) 7.54 (d, *J* = 8.0 Hz, 2H), 7.36-7.20 (m, 7H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 4.50 (d, *J* = 14.5 Hz, 1H), 4.48 (d, *J* = 1 Hz, 1H), 4.33 (q, *J* = 5.5 Hz, 2H), 4.17 (d, *J* = 14.5 Hz, 1H), 3.81-3.77 (m, 4H), 3.47-3.40 (m, 2H), 2.74-2.68 (m, 4H), 2.41 (s, 3H), 2.22 (m, 1H), 1.22 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.9, 159.1, 145.1, 137.9, 134.5, 130.8, 129.9, 129.2, 128.8, 128.4, 128.3, 127.6, 127.5, 113.7, 85.9, 72.7, 69.5, 63.5, 55.6, 55.2, 50.3, 39.0, 34.7, 21.7, 13.1. IR ($CHCl_3$, cm^{-1}): 2305, 1603. LRMS *m/z* (EI, 30 eV): 537 (0.25%), 121 (100%), 91 (94%).

4-Hydroxymethyl-6-methoxy-1-(4-methoxybenzyl)-3-methyl-5-(toluene-4-sulfonyl)-piperidine-2-one (7)

To a solution of methoxy lactam **6** (451 mg, 0.84 mmol) in 15 mL of MeOH was added a catalytic amount of Pd/C, and the reaction mixture was stirred under hydrogen overnight. After filtration of the catalyst, the solution was extracted with CH_2Cl_2 and washed with water. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude residue was subjected to flash silica gel chromatography (elution with hexane/ethyl acetate 2:1) to give 338 mg (90%) of **7**, pale yellow oil. ^1H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8 Hz, 2H), 7.35 (d, *J* = 8 Hz, 2H), 7.28 (d, *J* = 8 Hz, 2H), 6.87 (d, *J* = 8 Hz, 2H), 5.06 (d, *J* = 14.5 Hz, 1H), 4.87 (d, *J* = 1 Hz, 1H), 4.12 (d, *J* = 14.5 Hz, 1H), 3.80 (s, 3H), 3.77 (dd, *J* = 3.5, 1 Hz, 1H), 3.60 (d, *J* = 3.5 Hz, 1H), 2.75 (s, 3H), 2.67 (m, 1H), 2.46 (s, 3H), 2.23 (m, 1H), 1.26 (d, *J* = 7 Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.73, 159.20, 145.51, 134.33, 130.82 (2C), 130.12 (2C), 129.27, 128.77 (2C), 113.81 (2C), 85.64, 64.13, 62.86, 55.81, 55.25, 50.46, 40.43, 34.32, 21.70, 13.34. IR ($CHCl_3$, cm^{-1}): 2253, 1672. LRMS *m/z* (EI, 30 eV): 447 (5.54%), 260 (26.67%), 121 (100%). HRMS (EI, 30 eV) calcd for $C_{23}H_{29}NO_6S$ (M^+) 447.1713, found 447.1710.

2-Methoxy-1-(4-methoxybenzyl)-5-methyl-6-oxo-3-(toluene-4-sulfonyl)-piperidine-4-carbaldehyde (8)

A solution of **7** (551 mg, 1.23 mmole) in CH_2Cl_2 (15 mL) was added to a mixture of PCC (317 mg, 1.47 mmole) and Celite in CH_2Cl_2 (10 mL). The reaction mixture was stirred overnight at room temperature, then filtered over a short pad of silica gel with (hexane/ethyl acetate 4:1) to provide 466 mg (85%) of aldehyde **8**, pale yellow oil. ^1H NMR (500 MHz, $CDCl_3$): δ 9.54 (s, 1H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8 Hz, 2H), 4.98 (d, *J* = 14.5 Hz, 1H), 4.91 (d, *J* = 1.5 Hz, 1H), 4.27 (d, *J* = 14.5 Hz, 1H), 4.10 (dd, *J* = 5, 1.5 Hz, 1H), 3.81 (s, 3H), 2.94-2.77 (m, 2H), 2.77 (s, 3H), 2.46

(s, 3H), 1.40 (d, J = 7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.76, 171.85, 159.28, 145.84, 133.68, 130.85 (2C), 130.25 (2C), 130.00, 128.74 (2C), 113.86 (2C), 85.01, 62.06, 55.71, 55.24, 50.34, 49.47, 34.53, 21.70, 14.22. IR ($CHCl_3$, cm^{-1}): 2253, 1676. LRMS *m/z* (FAB): 446 (1.41%), 121 (100%). HRMS (FAB) calcd for $C_{23}H_{28}NO_6S$ (M^++1) 446.1637, found 446.1622.

1-(4-Methoxybenzyl)-3-methyl-2-oxo-1,2-dihydropyridine-4-carbaldehyde (9)

To a solution of aldehyde **8** (750 mg, 1.67 mmole) in 15 mL toluene was added DBU (1 mL, 6.70 mmol). The reaction mixture was stirred at 90 °C for 8 hrs, quenched with $NaHCO_3$ (25 mL) and extracted with AcOEt (3 × 20 mL). The organic layers were washed with brine, dried with anhydrous $MgSO_4$, filtered and evaporated. The residue was purified by column chromatography on silica gel (elution with hexane/ethyl acetate = 2:1) to provide 369 mg (86%) of pyridine-2-one **9**, pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.39 (s, 1H), 7.28-7.24 (m, 3H), 6.87 (d, J = 8.5 Hz, 2H), 6.52 (d, J = 7.0 Hz, 1H), 5.09 (s, 2H), 3.79 (s, 3H), 2.51 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 190.8, 163.5, 159.5, 139.2, 135.2, 134.2, 129.8 (2C), 127.8, 114.3 (2C), 101.7, 55.2, 52.4, 11.0. IR ($CHCl_3$, cm^{-1}): 1701, 1619. LRMS *m/z* (EI, 30 eV): 257 (20.39%), 121 (100%), 91 (32.55%). HRMS (EI, 30 eV) calcd for $C_{15}H_{15}NO_3$ (M^+) 257.1052, found 257.1052.

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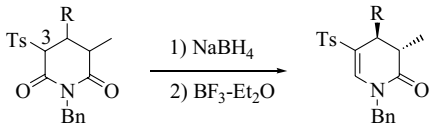
5. (a) We have performed the following chemistries on **3**; only one isomer was obtained in each case which indicated that each pair of stereoisomers of product **3** were C-3 epimer. The configuration of **10a** was elucidated by NOESY studies. There is no NOE effect between two methyl groups.



3 **10**

10a R = CH_3
10b R = CH_2OBn

(b) For **10a**: 85% yield; pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70 (d, J = 8.5 Hz, 2H), 7.36-7.22 (m, 8H), 4.83 (d, J = 15 Hz, 1H), 4.68 (d, J = 15 Hz, 1H), 2.47 (q, J = 7.5 Hz, 1H), 2.42 (s, 3H), 2.36 (q, J = 7.5 Hz, 1H), 0.98 (d, J = 7.5 Hz, 3H), 0.84 (d, J = 7.5 Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.88, 144.13, 136.98 (2C), 136.16, 129.74, 128.90, 128.08, 127.75, 127.51, 121.64, 49.79, 43.14, 33.89, 21.53, 18.88, 15.99. LRMS *m/z* (EI, 30 eV): 369 (11.57%), 91 (100%). HRMS calcd for $C_{21}H_{23}NO_3S$ 369.1399, found 369.1393. IR ($CHCl_3$, cm^{-1}): 2305, 1603. For **10b**: 86% yield; pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, J = 8.5 Hz, 2H), 7.38 (s, 1H), 7.33-7.18 (m, 12H), 4.81 (d, J = 15 Hz, 1H), 4.58 (d, J = 15 Hz, 1H), 4.30 (s, 2H), 3.40 (dd, J = 9.5, 3.5 Hz, 1H), 3.29 (dd, J = 9.5, 3.5 Hz, 1H), 2.86 (q, J = 7.5 Hz, 1H), 2.42-2.41 (m, 4H), 0.86 (d, J = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.00, 144.03, 139.23, 137.71, 137.11, 136.07, 129.70 (2C), 128.77 (2C), 128.32 (2C), 127.88 (2C), 127.63 (2C), 127.62 (2C), 127.55 (2C), 115.88, 73.17, 70.82, 49.71, 40.13, 39.10, 21.55, 16.63. LRMS *m/z* (EI, 30 eV): 476 (2.75%), 91 (100%). HRMS (FAB) calcd for $C_{28}H_{30}NO_4S$ (M^++1) 476.1894, found 476.1900. IR ($CHCl_3$, cm^{-1}): 1695, 1647.