Mannich-type Reactions of *in Situ* Generated *N*-Acyliminium Ions from α-Amido *p*-Tolylsulfones with Silyl Enolates

Sang-Hyeup Lee[*] and Santosh T. Kadam[*]

Department of Life Chemistry, Catholic University of Daegu, Gyeongsan 712-702, Korea
[*]E-mail: leeshh@cu.ac.kr (S.-H. Lee), stk2010@cu.ac.kr (S.T. Kadam)
Received July 6, 2011, Accepted August 30, 2011

Bismuth tribromide (BiBr₃) catalyzed Mannich-type reactions of *N*-acyliminium ions which generated *in situ* from *N*-benzyloxycarbonylamino *p*-tolylsulfones have been developed. In the presence of catalytic amount of BiBr₃, *N*-benzyloxycarbonylamino *p*-tolylsulfones prepared from aromatic and aliphatic aldehydes reacted with silyl enol ether and silyl enol ester under mild reaction conditions to afford *N*-Cbz-protected β-amino ketones and *N*-Cbz-protected β-amino esters in moderate to good yield, respectively.

Key Words : α-Amido *p*-tolylsulfone, Cbz-Protected β-amino ketone, *N*-Acyliminium ion, Mannich-type reaction

Introduction

A Mannich and Mannich-type reactions are powerful methods for the synthesis of β-amino carbonyl compounds and for fundamental carbon-carbon bond forming reaction in synthetic chemistry.[1] Due to the unique biological properties of the products, tremendous efforts have been made for the development of Mannich and Mannich-type reactions. β-Amino carbonyl compounds are important building blocks for the synthesis of natural products and pharmaceutical compounds.[2] They are also employed as intermediates in the synthesis of nitrogen containing biologically active compounds.[3] The classical Mannich reactions include the one-pot, three-component condensation of aldehyde, amine and enolizable ketone.[4] Another method which can provide expedient access to β-amino carbonyl compound is the reaction between preformed imine with enolizable ketone or silyl enolate.[5] However, the use of alkyl imines in Mannich reactions raises problem due to their instability. Imines and iminium ions can be converted to corresponding enamines through tautomerization, which can hamper the nucleophilic addition to imines or iminium ions.[6] Moreover, several functionalized imines are unstable under certain reaction conditions. These problems can be overcome by the use of *in situ* generated imines or iminium ions from stable precursor.

α-Amido *p*-tolylsulfones (*N*-benzyloxycarbonylamino *p*-tolylsulfones), which can be easily prepared by reaction of corresponding aldehyde, sodium *p*-toluenesulfinate and carbamate in presence of formic acid,[7] are considered as stable precursor of *N*-acyliminium ion. Under the influence of Lewis acid, α-amido *p*-tolylsulfones **I** are readily converted to the *N*-acyliminium ion **II** which further react with various nucleophiles to give corresponding Mannich products **III** (Scheme 1).[8]

Recently, the synthetic application of *N*-acyliminium ion has been employed in the synthesis of β-amino carbonyl compounds,[9a] α-amino nitriles,[9b] α-amino phosphonates,[9c] unsymmetrical and bis-symmetrical triarylmethanes,[9d-e] β-aminoketones[9f] and α-fluoro β-amino esters.[9g] Olivier *et al.* have demonstrated the efficient method for the synthesis of β-amino carbonyl compounds from *N*-alkoxycarbonylamino sulfones.[9h] Ballini *et al.* have shown the Friedel-Crafts reactions of α-amido sulfones for the synthesis of 3-substituted indoles.[9i] Gianelli *et al.* have utilized the amino catalyst for the *anti*-Mannich reaction of aldehydes with α-amido *p*-tolylsulfones.[9j]

According to the principle of green chemistry, synthetic method should be designed to use substances that exhibit little or no toxicity to human health and environment.[10] In this regard, bismuth salts have recently attracted considerable attention because they are remarkably nontoxic, stable and inexpensive.[11] Recently, bismuth salts has been widely used as catalyst for various organic transformations such as reductive coupling of carbonyl compounds with alkoxysilane,[12a] allylation of aldehyde,[12b] allylation of aldimine,[12c] silylation of alcohols[12d] and condensation of δ-hydroxy α,β-unsaturated aldehyde.[12e] In continuation of research work on Mannich-type reaction,[4h] herein we describe the BiBr₃ catalyzed Mannich-type reactions of *N*-benzyloxycarbonylamino *p*-tolylsulfones with silyl enol ether and ester.
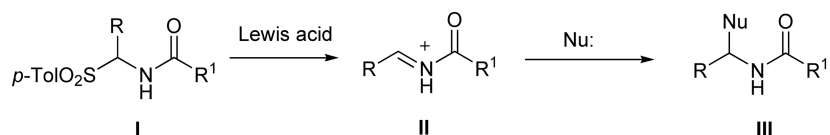
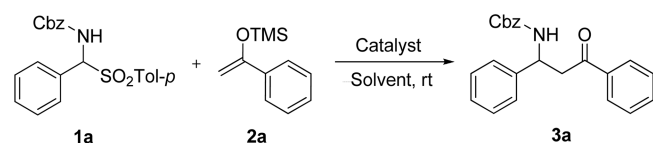**Scheme 1.** In situ generation of *N*-acyliminium ion from α-amido *p*-tolylsulfones.

Results and Discussions

The Mannich-type reaction of *N*-acyliminium ion, which generated *in situ* from *N*-benzyloxycarbonylamino phenyl *p*-tolylsulfones, with silyl enolates provided the corresponding *N*-benzyloxycarbonyl protected β-amino carbonyl compounds.

The optimization of reaction conditions has been performed using α-amido *p*-tolylsulfone **1a** and trimethyl (1-phenylvinyloxy)silane **2a** as model substrate in presence of various catalysts, as shown in Table 1. La(OTf)$_3$ and Yb(OTf)$_3$ gave the corresponding product in modest yield (58 and 43%, respectively) in 120 min reaction time using CH$_2$Cl$_2$ as solvent (Table 1, entries 1 and 2). Heterogeneous polymeric cation-exchange resin (Amberlyst-15) indicates no catalytic activity for this conversion (entry 3). Fortunately, BiBr$_3$ (10 mol %) shows 80% yield of desired product within 45 min reaction time in CH$_2$Cl$_2$ (entry 4). The catalytic activity of BiBr$_3$ was checked in other organic solvents such as THF, CH$_3$CN, MeOH and Et$_2$O, however improvement in terms of reaction time and product yield was not observed (entries 5-8). Increasing the catalyst loading to 20 mol % does not improve the reaction yield significantly, however reduction of catalyst loading (5 mol %) resulted in lowered yield (52%), even after prolonged reaction time (entries 9 and 10). Accordingly, we selected the BiBr$_3$ as catalyst for the rest of experiments and the use of 10 mol % of catalyst in CH$_2$Cl$_2$ as solvent were chosen to be the optimum reaction condition (entry 4).

The scope and applicability of this Mannich-type reaction were examined using various *N*-benzyloxycarbonylamino (*N*-Cbz-amino) *p*-tolylsulfones in combination with silyl enol ether and silyl ketene acetal. Variety of *N*-benzyloxycarbonylamino *p*-tolylsulfones **1** were prepared from corresponding aliphatic and aromatic aldehydes and in turn reacted with silyl enol ether **2a** to give the corresponding Cbz-protected β-amino ketones **3** in reasonable yield (Table 2, entries 1-8).

N-Cbz-amino phenyl *p*-tolylsulfone **1**, containing unsubstituted phenyl ring gave corresponding *N*-Cbz-protected β-amino ketone in 80% yield (entry 1). The reaction of **1** containing electron-donating methoxy and methyl substituents on their *p*-position of the phenyl ring underwent efficiently to provide the products in quite good yield (entries 2-3). Noteworthy is that the reaction of **1** containing aromatic ring substituted with electron-withdrawing chlorine

Table 1. Mannich-type reaction of *N*-benzyloxycarbonylamino phenyl *p*-tolylsulfone with trimethyl(1-phenylvinyloxy)silane[a]
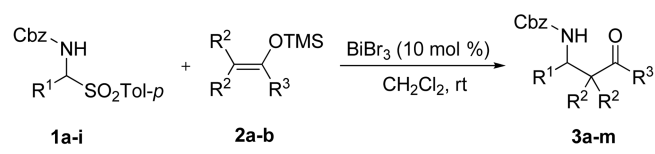

Entry	Catalyst (mol %)	Solvent	Time (min)	Yield (%)[b]
1	La(OTf)$_3$ (10)	CH$_2$Cl$_2$	120	58
2	Yb(OTf)$_3$(10)	CH$_2$Cl$_2$	120	43
3	Amberlyst-15 (50 mg)	CH$_2$Cl$_2$	120	NR
4	BiBr$_3$(10)	CH$_2$Cl$_2$	45	80
5	BiBr$_3$(10)	THF	60	48
6	BiBr$_3$(10)	CH$_3$CN	120	40
7	BiBr$_3$(10)	MeOH	175	27
8	BiBr$_3$(10)	Et$_2$O	180	39
9	BiBr$_3$(20)	CH$_2$Cl$_2$	40	80
10	BiBr$_3$(5)	CH$_2$Cl$_2$	120	52

[a]Reagent and conditions: 1 mmol of α-Amido *p*-tolylsulfones **1a**, 1.2 mmol of trimethyl(1-phenylvinyloxy)silane **2a** and X mol % of catalyst were employed for the reaction (given in parenthesis). [b]Isolated yield.

Table 2. BiBr$_3$-catalyzed Mannich-type reaction of *N*-benzyloxycarbonylamino phenyl *p*-tolylsulfone **1a** with silyl enol ether and ester[a]

Entry	R	R^1 and R^2	R^3	3	Time (min)	Yield (%)[b]
1		H	Ph	**3a**	45	80
2	MeO—	H	Ph	**3b**	30	85
3	Me—	H	Ph	**3c**	30	86
4	Cl—	H	Ph	**3d**	60	72
5	Cl— (ortho)	H	Ph	**3e**	60	61
6		H	Ph	**3f**	40	80
7		H	Ph	**3g**	80	72
8		H	Ph	**3h**	180	64
9		Me	OMe	**3i**	70	77
10	MeO—	Me	OMe	**3j**	60	82
11	Me—	Me	OMe	**3k**	60	80
12	Cl—	Me	OMe	**3l**	80	71
13		Me	OMe	**3m**	120	66

[a]Reagent and conditions: 1 mmol of α-Amido *p*-tolylsulfones **1a-i**, 1.2 mmol of silyl enolates **2a-b** and 10 mol % of BiBr$_3$ were employed for the reaction in CH$_2$Cl$_2$ (4 mL). [b]Isolated yield.

substituent required quite longer reaction time and provided the corresponding products in slightly lowered yield (entries 4 and 5). This indicates that the electronic effect of chlorine atom may play an important role on Mannich reaction. Again, *N*-Cbz-amino phenyl *p*-tolylsulfone **1** derived from piperonal reacted with silyl enol ether **2a** smoothly to provide corresponding β-amino ketone **3** in good yield (entry 6).

This catalytic protocol also worked efficiently when *N*-Cbz-amino alkyl *p*-tolylsulfone **1**, where R = alkyl groups, were utilized as substrates (entries 7 and 8). Although the yields were moderate and longer reaction time was required, *N*-Cbz-amino alkyl *p*-tolylsulfones **1**, prepared from aliphatic aldehydes, was transformed to corresponding β-amino ketones **3**.

We extend present catalytic protocol for the Mannich-type reaction of *N*-Cbz-amino phenyl *p*-tolylsulfone **1** with tetra substituted silyl ketene acetal **2b**. Fortunately, it was equally effective for the production of Cbz-protected β-amino ester in good yield under the same reaction conditions (Table 2, entries 9-13). *N*-Cbz-amino phenyl *p*-tolylsulfone **1** containing electron-donating groups (entries 10-11) as well as electron-withdrawing chlorine substituents (entry 12) reacted to give corresponding ester in good yield. This BiBr$_3$ catalyzed reaction protocol also tolerated the existence of basic heteroaromatic pyridine functionality (entry 13).

Conclusions

In conclusion, a mild and efficient catalytic method has been developed for the synthesis of Cbz-protected β-amino ketones and esters through Mannich-type reactions of α-amido *p*-tolylsulfones, which are precursors of *N*-acyliminium ion, with silyl enolates. α-Amido *p*-tolylsulfones **I** derived from various types of aldehydes are coupled with silyl enol ether and silyl ketene acetal using BiBr$_3$ as an efficient catalyst to give corresponding Cbz-protected β-amino carbonyl compounds. BiBr$_3$ were found to be remarkably nontoxic, stable and inexpensive catalyst for Mannich-type reaction between α-amido *p*-tolylsulfones and silyl enol ether/ester.

Experimental Section

The α-Amido *p*-tolylsulfones **1** were prepared from the corresponding aldehydes by the literature method.[7] The ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra were recorded with Varian VNS600 spectrometer. Chemical shifts were reported in ppm in CDCl$_3$ with tetramethylsilane as the internal standard. MS spectra were recorded on an Agilent Technologies GC-MS instrument equipped with a 7890 injector, 5975 mass selective detector. The mass spectrometer was operated in EI mode at 70 eV and MS spectra were recorded from *m/z* 50 to 650.

General Procedure for Mannich-type Reactions of α-amido *p*-tolylsulfones with Silyl Enolates. To a mixture of α-amido *p*-tolylsulfones (1 mmol) and BiBr$_3$ (10 mol %) in

CH$_2$Cl$_2$ (4 mL), silyl enolates (1.2 mmol) was added at rt. The progress of the reaction was monitored by TLC. After the completion of reaction, water was added and reaction mixture was extracted with EtOAc. Concentration of the organic layer under vacuum gave crude mass, which was then purified by flash chromatography on silica gel to give the corresponding products.

All products were characterized by ^{1}H and ^{13}C NMR, and the data are consistent with literature values.[9h,4i-j] ^{1}H and ^{13}C NMR data for the new compounds **3e-m** (Table 2, entries 5-13) are given below.
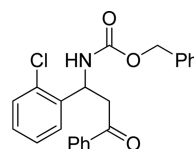

Compound 3e: ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.87 (d, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 6.8 Hz, 2H), 7.44-7.10 (m, 8H), 6.25 (brs, 1H), 5.62 (m, 1H), 5.08 (m, 2H), 3.68 (d, *J* = 14.7 Hz, 1H), 3.46 (d, *J* = 15.5 Hz, 1H). ^{13}C NMR (150 MHz, CDCl$_3$): 198.1, 155.5, 138.4, 136.4, 136.3, 133.5, 132.3, 129.8, 128.7, 128.6, 128.4, 128.3, 128.1, 127.0, 66.8, 49.6, 41.8; MS (EI) *m/z* M$^+$ for C$_{23}$H$_{20}$ClNO$_3$ calc. 393, found 393 (M$^+$), 394 (M + 1), 395 (M + 2), 358, 258, 91.
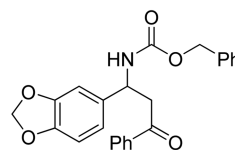

Compound 3f: ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.88 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.36-7.20 (m, 5H), 6.84 (s, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 5.90 (s, 2H), 5.82 (brs, 1H), 5.22 (q, *J* = 6.7 Hz, 1H), 5.12-5.04 (m, 2H), 3.63 (d, *J* = 15.5 Hz, 1H), 3.38 (dd, *J* = 16.7, 6.1 Hz, 1H). ^{13}C NMR (150 MHz, CDCl$_3$): 197.9, 155.6, 147.9, 146.9, 136.6, 136.4, 135.3, 133.4, 128.7, 128.5, 128.1, 119.7, 108.3, 107.1, 101.1, 66.8, 51.7, 44.1; MS (EI) *m/z* M$^+$ for C$_{24}$H$_{21}$NO$_5$ calc. 403, found 403 (M$^+$), 312, 295, 268, 105.
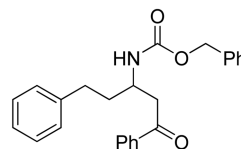

Compound 3g: ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.91 (d, *J* = 7.4 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.38-7.05 (m, 10H), 5.49 (brd, *J* = 5.6 Hz, 1H), 5.09 (m, 2H), 4.20-4.10 (m, 1H), 3.34 (dd, *J* = 17.0, 4.2 Hz, 1H), 3.14 (dd, *J* = 17.0, 5.4 Hz, 1H), 2.80-2.70 (m, 1H), 2.69-2.60 (m, 1H), 2.14-2.00 (m, 1H), 1.96-1.85 (m, 1H). ^{13}C NMR (150 MHz, CDCl$_3$): 198.8, 156.0, 141.4, 136.9, 136.6, 133.4, 128.7, 128.5, 128.44, 128.37, 128.08, 128.07, 128.0, 126.0, 66.6, 48.3, 42.6, 35.9, 32.8; MS (EI) *m/z* M$^+$ for C$_{25}$H$_{25}$NO$_3$ calc. 387, found 387 (M$^+$), 388 (M + 1), 296, 235, 105.
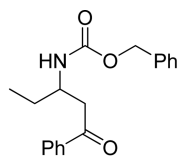
Compound 3h: ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.94 (d, J = 7.4 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.4 Hz, 2H), 7.38-7.25 (m, 5H), 5.35 (d, J = 6.9 Hz, 1H), 5.13-5.03 (m, 2H), 4.08-3.98 (m, 1H), 3.34 (dd, J = 16.6, 4.3 Hz, 1H), 3.11 (dd, J = 16.7, 5.7 Hz, 1H), 1.70-1.60 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H). ^{13}C NMR (150 MHz, CDCl$_3$): 198.8, 156.0, 136.9, 136.6, 133.3, 128.6, 128.4, 128.03, 127.97, 127.9, 66.5, 49.9, 42.1, 27.2, 10.7; MS (EI) m/z M$^+$ for C$_{19}$H$_{21}$NO$_3$ calc. 311, found 311 (M$^+$), 312 (M + 1), 204, 176, 105, 91.
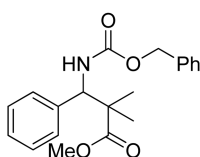
Compound 3i: ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.40-7.24 (m, 8 H), 7.19 (d, J = 7.3 Hz, 2H), 6.34 (d, J = 9.0 Hz, 1H), 5.09 (d, J = 12.2 Hz, 1H), 5.01 (d, J = 12.4 Hz, 1H), 4.74 (d, J = 9.5 Hz, 1H), 3.62 (s, 3H), 1.31 (s, 3H), 1.11 (s, 3H). ^{13}C NMR (150 MHz, CDCl$_3$): 176.7, 155.8, 139.1, 136.4, 128.4, 128.1, 128.02, 128.00, 127.7, 127.6, 66.7, 62.2, 51.9, 46.5, 24.6, 22.5; MS (EI) m/z M$^+$ for C$_{20}$H$_{23}$NO$_4$ calc. 341, found 341 (M$^+$), 342 (M + 1), 240, 196, 91.
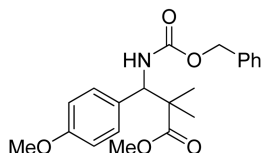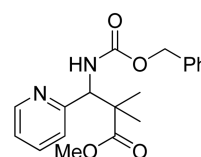
Compound 3j: ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.40-7.20 (m, 5H), 7.12 (d, J = 8.2 Hz, 2H), 6.81 (d, J = 8.6 Hz, 2H), 6.34 (d, J = 6.4 Hz, 1H), 5.09 (d, J = 12.3 Hz, 1H), 5.00 (d, J = 12.3 Hz, 1H), 4.72 (brd, J = 9.2 Hz, 1H), 3.74 (s, 3H), 3.61 (s, 3H), 1.29 (s, 3H), 1.11 (s, 3H). ^{13}C NMR (150 MHz, CDCl$_3$): 176.7, 158.8, 155.7, 136.4, 131.2, 128.6, 128.3, 127.90, 127.86, 113.3, 66.5, 61.5, 55.0, 51.8, 46.6, 24.4, 22.3; MS (EI) m/z M$^+$ for C$_{21}$H$_{25}$NO$_5$ calc. 371, found 371 (M$^+$), 270, 162, 91.
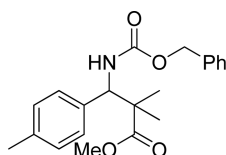
Compound 3k: ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.37-7.25 (m, 5H), 7.12-7.05 (m, 4H), 6.34 (d, J = 8.1 Hz, 1H), 5.10 (d, J = 12.3 Hz, 1H), 5.01 (d, J = 12.3 Hz, 1H), 4.74 (brd, J = 9.4 Hz, 1H), 3.63 (s, 3H), 2.31 (s, 3H), 1.31 (s, 3H), 1.13 (s, 3H). ^{13}C NMR (150 MHz, CDCl$_3$): 176.7, 155.7, 137.1, 136.4, 136.1, 128.7, 128.3, 128.0, 027.9, 127.5, 66.6, 61.8, 51.8, 46.5, 24.4, 22.4, 20.9; MS (EI) m/z M$^+$ for C$_{21}$H$_{25}$NO$_4$ calc. 355, found 355 (M$^+$), 254, 210, 146, 91.
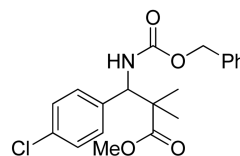
Compound 3l: ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.35-7.25 (m, 5H), 7.24 (d, J = 8.3 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 6.36 (d, J = 8.8 Hz, 1H), 5.08 (d, J = 12.2 Hz, 1H), 5.00 (d, J = 12.2 Hz, 1H), 4.68 (d, J = 9.2 Hz, 1H), 3.62 (s, 3H), 1.31 (s, 3H), 1.09 (s, 3H). ^{13}C NMR (150 MHz, CDCl$_3$): 176.5, 155.8, 137.8, 136.3, 133.4, 129.1, 128.4, 128.3, 128.08, 128.05, 66.8, 61.7, 52.0, 46.3, 24.7, 22.5; MS (EI) m/z M$^+$ for C$_{20}$H$_{22}$ClNO$_4$ calc. 375, found 375 (M$^+$), 376 (M + 1), 377 (M + 2), 274, 230, 91.

Compound 3m: ^{1}H NMR (600 MHz, CDCl$_3$): δ 8.47 (d, J = 4.4 Hz, 1H), 7.58 (t, J = 7.6 Hz, 1H), 7.40-7.20 (m, 5H), 7.18 (d, J = 7.7 Hz, 1H), 7.13 (dd, J = 7.1, 5.2 Hz, 1H), 6.42 (d, J = 9.4 Hz, 1H), 5.10 (d, J = 12.2 Hz, 1H), 5.04 (d, J = 12.4 Hz, 1H), 4.97 (d, J = 9.6 Hz, 1H), 3.64 (s, 3H), 1.20 (s, 3H), 1.17 (s, 3H). ^{13}C NMR (150 MHz, CDCl$_3$): 176.5, 157.5, 156.2, 148.9, 136.5, 136.1, 128.4, 128.0, 123.3, 122.6, 66.8, 61.5, 51.9, 46.8, 22.8, 22.5; MS (EI) m/z M$^+$ for C$_{19}$H$_{22}$N$_2$O$_4$ calc. 342, found 342 (M$^+$), 343 (M + 1), 241, 197, 107, 91.

Supplementary Information. ^{1}H and ^{13}C NMR spectra of the new compounds **3e-m**. It is available through the Internet http://journal.kcsnet.or.kr.

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