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STEREOSELECTIVE SYNTHESIS OF (2E)-CINNAMANILIDES *via* DESULFONYLATION OF (2E)- α -AMIDO- α , β -UNSATURATED SULFONES BY SAMARIUM/GLACIAL ACETIC ACID/ETHANOL SYSTEM

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STEREOSELECTIVE SYNTHESIS OF (2E)-CINNAMANILIDES *via*
DESULFONYLATION OF (2E)- α -AMIDO- α , β -UNSATURATED SULFONES BY
SAMARIUM/GLACIAL ACETIC ACID/ETHANOL SYSTEM

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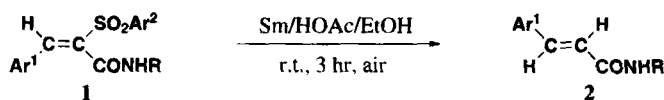
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Sulfone compounds are useful intermediates¹ and the desulfonylation of sulfones is an important reaction in organic synthesis.² A wide variety of reagents have been used for desulfonylation, *e. g.* sodium amalgam-disodium hydrogen phosphate system,³ aluminium amalgam,⁴ lithium-ethylamine system,⁵ lithium aluminium hydride-copper (II) chloride system,⁴ tri-*n*-butylstannane-AIBN (azobisisobutyronitrile),^{2b} sodium hydrogen telluride,⁶ samarium diiodide,⁷ zinc-titanium (IV) chloride system,⁸ and samarium-mercury (II) chloride system,⁹ etc. However, these reagents have one or more limitations with regard to general applicability, ready availability, selectivity, operational convenience and toxicity. For instance, samarium diiodide, zinc-titanium (IV) chloride system, and samarium-mercury (II) chloride system need delicate treatment under a nitrogen atmosphere because low valent samarium and titanium are very sensitive to air oxidation; the use of toxic mercury (II) chloride cannot be avoided when sodium amalgam, aluminium amalgam and samarium-mercury (II) chloride system are used; besides, sodium hydrogen telluride and tri-*n*-butylstannane are themselves dangerous or toxic; samarium diiodide and sodium hydrogen telluride can induce both desulfonylation and reduction of double bond for unsaturated compounds. As a result, there is still considerable interest in finding more effective and convenient methods for desulfonylation.

On the other hand, though samarium diiodide and organosamarium compounds have been widely employed as useful reagents in organic synthesis,¹⁰ there are relatively few reports¹¹ on the direct use of samarium metal in organic synthesis because the surface of samarium metal is inactive. In order to improve the reactivity of samarium, some additives such as mercury (II) chloride,¹² chlorotrimethylsilane,¹³ or ammonium chloride (aq.)¹⁴ have been used for this purpose. Herein we report samarium-glacial acetic acid-ethanol system, which is a new reducing system, could induce effective desulfonylation toward (2E)- α -amido- α , β -unsaturated sulfones to afford (2E)-cinnamanilides in moderate to good yields under mild conditions.

The results are summarized in the **Table**. The reaction gave excellent chemoselectivity as well as stereoselectivity. The experimental results showed that, upon reaction of α -amido- α , β -unsaturated sulfones with the samarium-glacial acetic acid-ethanol system, reductive desulfonylation took place to give α , β -unsaturated amides but the conjugated C=C double bond remaining unaffected; besides, starting from (2E)- α -amido- α , β -unsaturated sulfones **1**, desulfonylation afforded E-isomers

(with 100% stereospecificity) of cinnamanilides **2** only. The reaction could still give good yields without the protection of nitrogen atmosphere; it could be carried out in open air, a fact which adds much convenience to the present procedure. Attempts to carry out the reaction in aqueous media (by addition of 0.5 mL water into reaction mixture) were unavailing due to the poor yields of the products.



a) Ar¹ = C₆H₅, R = C₆H₅, Ar² = C₆H₅, b) Ar¹ = *p*-CH₃C₆H₄, R = C₆H₅, Ar² = C₆H₅, c) Ar¹ = *p*-CH₃OC₆H₄, R = C₆H₅, Ar² = C₆H₅, d) Ar¹ = *p*-ClC₆H₄, R = C₆H₅, Ar² = C₆H₅, e) Ar¹ = C₆H₅, R = *n*-C₇H₁₅, Ar² = *p*-CH₃C₆H₄, f) Ar¹ = *p*-CH₃C₆H₄, R = *n*-C₇H₁₅, Ar² = *p*-CH₃C₆H₄, g) Ar¹ = *p*-CH₃OC₆H₄, R = *n*-C₇H₁₅, Ar² = *p*-CH₃C₆H₄, h) Ar¹ = *p*-ClC₆H₄, R = *n*-C₇H₁₅, Ar² = *p*-CH₃C₆H₄.

In summary, it has been found that samarium-glacial acetic acid-ethanol system could effectively induce desulfonylating reaction toward (2*E*)- α -amido- α,β -unsaturated sulfones to give stereoselective products of (2*E*)-cinnamanilides. The notable advantages of this reaction are its mild conditions, simple operation and high yields

Table. Yields, Mps., Elemental Analysis and Spectral Data of Compounds **2**

Cmpd	Yield (%)	mp. (°C) (<i>lit.</i> mp.)	IR (cm ⁻¹)	¹ H NMR (δ)	Elemental Analysis (Found)			MS m/z (M ⁺)
					C	H	N	
2a	86	150-151 20 ^a (151-152 ¹⁵) (149 ¹⁶)	1665, 1630	7.78 (d, 1H, J=15.6 Hz), 7.70-7.04 (m, 11H, ArH, NH), 6.70 (d, 1H, J=15.6 Hz)	--	--	--	--
2b	84	169-170	1654 1628	7.82 (d, 1H, J=15.6 Hz), 7.71-7.04 (m, 10H, ArH, NH), 6.55 (d, 1H, J=15.6 Hz), 2.30 (s, 3H)	80.98 (80.90)	6.37 (6.28)	5.90 (5.96)	237
2c	79	141-142 (140 ¹⁷)	1654 1627	7.80 (d, 1H, J=15.6 Hz), 7.72-7.06 (m, 10H, ArH, NH), 6.56 (d, 1H, J=15.6 Hz), 3.74 (s, 3H)	--	--	--	--
2d	83	183-184 (183 ¹⁶)	1662 1632	7.76 (d, 1H, J=15.6 Hz), 7.68-7.10 (m, 10H, ArH, NH), 6.67 (d, 1H, J=15.6 Hz)	--	--	--	--
2e	80	60-61 (58.8-59.8 ¹⁸)	1653 1628	7.68 (d, 1H, J=15.6 Hz), 7.64-7.10 (m, 5H, ArH), 6.34 (d, 1H, J=15.6 Hz), 5.90 (br., 1H, NH), 3.07 (m, 2H), 1.85-1.12 (m, 10H), 0.85 (t, 3H, J=8.0 Hz)	--	--	--	--

Table. Continued...

Cmpd	Yield (%)	mp. (°C) (lit. mp.)	IR (cm ⁻¹)	¹ H NMR (δ)	Elemental Analysis (Found)			MS m/z (M ⁺)
					C	H	N	
2f	78	98-99	1652 1630	7.62 (d, 1H, J=15.6 Hz), 7.58-7.00 (m, 4H, ArH), 6.38 (d, 1H, J=15.6 Hz), 5.96 (br., 1H, NH), 3.10 (m, 2H), 2.30 (s, 3H), 1.86-1.10 (m, 10H), 0.85 (t, 3H, J=8.0 Hz)	78.72 (78.66)	9.71 (9.78)	5.40 (5.35)	259
2g	76	79-80	1656 1628	7.70 (d, 1H, J=15.6 Hz), 7.64-7.04 (m, 4H, ArH), 6.32 (d, 1H, J=15.6 Hz), 5.90 (br., 1H, NH), 3.76 (s, 3H), 3.08 (m, 2H), 1.84-1.14 (m, 10H), 0.85 (t, 3H, J=8.0 Hz)	74.14 (74.20)	9.15 (9.21)	5.09 (5.02)	275
2h	80	119-120	1650 1632	7.68 (d, 1H, J=15.6 Hz), 7.58-7.00 (m, 4H, ArH), 6.40 (d, 1H, J=15.6 Hz), 5.85 (br., 1H, NH), 3.10 (m, 2H), 1.84-1.13 (m, 10H), 0.85 (t, 3H, J=8.0 Hz)	68.68 (68.75)	7.92 (7.86)	5.09 (5.15)	279

^aThe yield was obtained when 0.5 mL water was added into reaction mixture.

EXPERIMENTAL SECTION

Mps are uncorrected. (2E)- α -Amido- α,β -unsaturated sulfones are easily prepared according to a reported procedure.¹⁹ Infrared spectra were recorded on a Bruker Vector 22 spectrometer in KBr with absorption in cm⁻¹. ¹H NMR spectra were determined in a Bruker AC-80 spectrometer as CDCl₃ solutions. J values are in Hz. Chemical shifts are expressed in δ downfield from internal tetramethylsilane. Mass spectra were recorded on a HP 5989B MS spectrometer. Microanalysis was carried out on a Carlo Erba EA 1110 instrument.

General Procedure. - Samarium powder (0.375 g, 2.5 mmol), glacial acetic acid (2 mL), ethanol (0.6 mL), THF (2 mL) and α -amido- α,β -unsaturated sulfones **1** (1 mmol) were placed in a 50 mL three-necked flask and the mixture was stirred at room temperature for 3 h. The mixture was filtered to remove the remaining samarium, the filtrate was extracted with diethyl ether (30 mL x 3) and washed with brine (20 mL x 2). After drying over MgSO₄, the solvent was evaporated *in vacuo* and the crude products were purified by preparative TLC on silica gel using cyclohexane-ethyl acetate (4:1) as eluent.

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REFERENCES

1. a) P. E. Magnus, *Tetrahedron*, **33**, 2019 (1977); b) B. M. Trost, *Bull. Chem. Soc. Jpn*, **61**, 107 (1988); c) N. S. Simpkin, *Tetrahedron*, **46**, 6951 (1990).
2. a) J. Bremner, M. Julia, M. Launay and J. P. Stacino, *Tetrahedron Lett.*, **23**, 3265 (1982); b) A. B. Smith, III, K. J. Hale and J. P. McCauley, Jr., *ibid.*, **30**, 5579 (1989).
3. a) B. M. Trost, H. C. Arndt, P. E. Strege and T. R. Verhoeven, *ibid.*, **18**, 3477 (1976); b) N. Satyamurthi, J. Singh and I. S. Aidhen, *Synthesis*, 375 (2000).
4. V. Pascali and A. Umani-Ronchi, *Chem. Commun.*, 351 (1973).
5. P. A. Grieco and Y. Masaki, *J. Org. Chem.*, **39**, 2135 (1974).
6. X. Huang and H. Z. Zhang, *Synth. Commun.*, **19**, 97 (1989).
7. H. Guo and Y. Zhang, *ibid.*, **30**, 1879 (2000).
8. H. Guo, S. Ye, J. Wang and Y. Zhang, *J. Chem. Res. (S)*, 114 (1997).
9. H. Guo and Y. Zhang, *Synth. Commun.*, **30**, 2559 (2000).
10. a) H.B. Kagan and J. L. Namy, *Tetrahedron*, **42**, 6573 (1986); b) G. A. Molander, *Chem. Rev.*, **92**, 29 (1992); c) G. A. Molander, *Org. React.*, **46**, 211 (1994); d) G. A. Molander and C. R. Harris, *Chem. Rev.*, **96**, 307 (1996).
11. a) R. Yanada, N. Negoro, K. Yanada and T. Fujita, *Tetrahedron Lett.*, **38**, 3271 (1997); b) M. Lautens, P. H. Delanghe, *J. Org. Chem.*, **60**, 2474 (1995).
12. G. A. Molander and L. S. Harring, *ibid.*, **54**, 3525 (1989).
13. L. Wang and Y. Zhang, *Tetrahedron*, **54**, 11129 (1998).
14. L. Wang and Y. Zhang, *Tetrahedron Lett.*, **39**, 5257 (1998).
15. Beistein, *I2*, 279.
16. J. Mirek, Z. Nauk and U. Jagiellon, *Pr. Chem.*, 61 (1965); *CA.*, **59**, 6226g (1965).
17. G. S. Ahluwalia, M. A. Haq and J. N. Ray, *J. Chem. Soc.*, 2059 (1931).
18. D. J. Currie and H. L. Holmes, *Can. J. Chem.*, **48**, 1340 (1970).
19. B. Gerhard and C. Bieter, *Chem. Ber.*, **106**, 2758 (1973).