OBC
www.rsc.org/obc

DABCO catalyzed addition of selenosulfonates to α,β-unsaturated ketones†

Yong-Ling Shi and Min Shi*
State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai, 200032, China.
E-mail: mshi@pub.sioc.ac.cn

Received 7th February 2005, Accepted 8th March 2005
First published as an Advance Article on the web 16th March 2005

In the presence of DABCO (30 mol%), the addition of various selenosulfonates to α,β-unsaturated ketones proceeded smoothly to give the corresponding adducts in good yields under mild conditions.

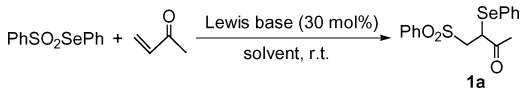
Recently, we have been investigating on the Baylis–Hillman reaction of aldehydes and *N*-tosylated imines (ArCH=NTs) with activated olefins in the presence of a variety of nitrogen and phosphine Lewis bases.[1–3] In this paper, we wish to report a novel DABCO (1,4-diazabicyclic[2,2,2]octane) catalyzed addition of selenosulfonates to α,β-unsaturated ketones to give the corresponding adducts in good yields under mild conditions.

The addition of selenosulfonates to olefins and other carbon–carbon unsaturated bonds has been known to proceed in the presence of Lewis acid $BF_3{\cdot}OEt_2$ or through a radical reaction pattern with either photochemical initiation, or upon heating with a radical initiator such as AIBN.[4,5] However, for α,β-unsaturated ketones such as methyl vinyl ketone (MVK), no reactions occurred under these reaction conditions. During our ongoing investigation on the Baylis–Hillman reaction, we found that many nitrogen Lewis bases could catalyze the addition of selenosulfonates to MVK to give the corresponding adduct **1a** in good yields at room temperature. The results are summarized in Table 1. In the presence of DABCO (30 mol%), **1a** was obtained in 81% yield after 1 h in THF in the reaction of selenosulfonate ($PhSeSO_2Ph$) with 2.0 eq. MVK (Table 1, entry 1). Using 4-dimethylamino-pyridine (DMAP) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as Lewis base catalysts, this reaction proceeded quickly, but **1a** was formed in 39 and 25% yields, respectively (Table 1, entries 2 and 3). Triethylamine (Et_3N) also can promote this reaction to give the adduct **1a** in 42% yield after 24 h under the similar conditions (Table 1, entry 4). Phosphine Lewis bases such as triphenylphosphine, diphenylmethylphosphine, dimethylphenylphosphine, tributylphosphine and trimethylphosphine showed no catalytic abilities for this reaction (Table 1, entries 5–9). The solvent effects have been examined by use of DABCO in toluene, ethanol, dichloromethane and ether (Et_2O). We found that THF is the solvent of choice (Table 1, entries 10–13).

Under the optimized reaction conditions, we next examined the addition of a variety of selenosulfonates to α,β-unsaturated ketones. The results are summarized in Table 2. We found that all these reactions proceeded smoothly under mild conditions to give the corresponding adducts **1b–l** in good to high yields after 1 h (Table 1, entries 1–11). It should be noted that for a branched α,β-unsaturated ketone (R = ^{i}Pr), the corresponding adducts **1d**, **1h** and **1l** were obtained in high yields as well (Table 1, entries 3, 7, and 11).

Their structures are determined by ^{1}H and ^{13}C NMR spectroscopic data, HRMS, and microanalyses (refer to the supplementary information). The obtained adducts **1** can undergo a selenoxide elimination upon oxidation with hydrogen peroxide in THF to afford the corresponding (*E*)-β-phenylsulfonylenones **2** within 1 h in high yields (Scheme 1).[6]

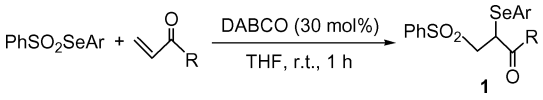
Table 1 Lewis base-catalyzed addition of selenosulfonate (1.0 eq.) to MVK (2.0 eq.)



Entry	Lewis base	Solvent	Time/h[b]	Yield/%[a] **1a**
1	DABCO	THF	1	81
2	DMAP	THF	1/2	39
3	DBU	THF	1/6	25
4	Et_3N	THF	24	42
5	PPh_3	THF	24	No reaction
6	PPh_2Me	THF	24	No reaction
7	$PPhMe_2$	THF	24	No reaction
8	PBu_3	THF	24	Trace
9	PMe_3	THF	24	Trace
10	DABCO	Toluene	2/3	39
11	DABCO	EtOH	1/2	—[c]
12	DABCO	CH_2Cl_2	1/2	59
13	DABCO	Et_2O	1/2	44

[a] Isolated yields. [b] The reaction time to consume all of the starting materials. [c] Complex reaction from which no products could be identified.

Table 2 DABCO-catalyzed addition of selenosulfonates (1.0 eq.) to α β-unsaturated ketones (2.0 eq.)

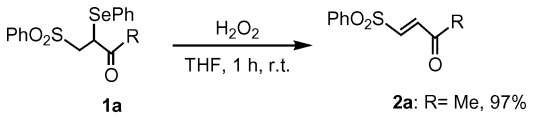


Entry	Ar	R	Yield /%[a] **1**
1	C_6H_5	Et	**1b**, 81
2	C_6H_5	Ph	**1c**, 75
3	C_6H_5	*i*-Pr	**1d**, 83
4	*p*-MeC_6H_4	Me	**1e**, 87
5	*p*-MeC_6H_4	Et	**1f**, 85
6	*p*-MeC_6H_4	Ph	**1g**, 85
7	*p*-MeC_6H_4	*i*-Pr	**1h**, 80
8	*p*-$MeOC_6H_4$	Me	**1i**, 90
9	*p*-$MeOC_6H_4$	Et	**1j**, 93
10	*p*-$MeOC_6H_4$	Ph	**1k**, 70
11	*p*-$MeOC_6H_4$	*i*-Pr	**1l**, 94

[a] Isolated yields.

† Electronic supplementary information (ESI) available: spectroscopic data, HRMS, analytical data, experimental procedures. See http://www.rsc.org/suppdata/ob/b5/b501942g/

DOI: 10.1039/b501942g

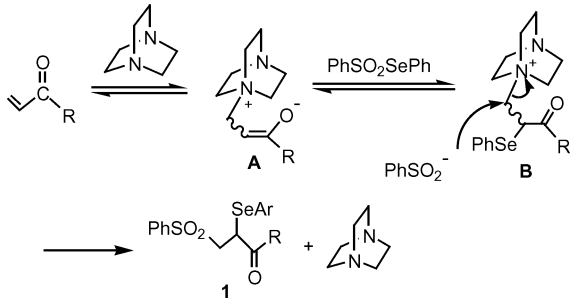


1a **2a**: R= Me, 97%

2b: R= Et, 99%, **2c**: R= Ph, 98%, **2d**: R= ^{i}Pr, 99%.

Scheme 1 Selenoxide elimination with hydrogen peroxide.

The mechanism for this unusual DABCO catalysed addition reaction of selenosulfonates to α,β-unsaturated ketones has not been unequivocally established, but on the basis of previous investigations[4] and the generally accepted reaction mechanism for Baylis–Hillman reaction,[1–3] one plausible explanation is proposed in Scheme 2. The nucleophilic addition of the *in situ* formed zwitterionic enolate **A**, derived from DABCO and the corresponding α,β-unsaturated ketone, to the selenosulfonate produces the intermediate **B**. The generated $PhSO_2^-$ species attacks at the terminal carbon of α,β-unsaturated ketones of the intermediate **B** to give the final product and regenerate DABCO Lewis base catalyst (Scheme 2).[7]



Scheme 2 The plausibel reaction mechanism.

The control experiment has confirmed that this addition reaction under the optimized conditions was unaffected by the addition of the radical inhibitors such as TEMPO and 3 eq. 2,6-di-*tert*-butyl-4-methylphenol (BHT), rendering unlikely the intervention of a radical pathway.

In conclusion, we have found a novel DABCO catalyzed addition of selenosulfonates to a variety of α,β-unsaturated ketones to give the adducts **1** in good to high yields within short reaction time under mild conditions. This synthetic approach also provides a facile route to the synthesis of (*E*)-β-phenylsulfonylenones **2**. Efforts are in progress to elucidate the mechanistic details of this reaction and to disclose its scope and limitations.

Acknowledgements

We thank the State Key Project of Basic Research (Project 973, No. G2000048007), Shanghai Municipal Committee of Science and Technology, Chinese Academy of Sciences (KGCX2-210-01), and the National Natural Science Foundation of China for financial support (20025206, 203900502, and 20272069).

Notes and references

1 For reviews on the Baylis–Hillman reaction: (*a*) E. Ciganek, *Org. React.*, 1997, **51**, 201–350; (*b*) D. Basavaiah, P. D. Rao and R. S. Hyma, *Tetrahedron*, 1996, **52**, 8001–8062; (*c*) D. Basavaiah, A. J. Rao and T. Satyanarayana, *Chem. Rev.*, 2003, **103**, 811–892.

2 (*a*) M. Shi, J.-K. Jiang and Y.-S. Feng, *Org. Lett.*, 2000, **2**, 2397–2400; (*b*) M. Shi and Y.-S. Feng, *J. Org. Chem.*, 2001, **66**, 406–411; (*c*) M. Shi, C.-Q. Li and J.-K. Jiang, *Chem. Commun.*, 2001, 833–834.

3 (*a*) M. Shi and Y.-M. Xu, *Chem. Commun.*, 2001, 1876–1877; (*b*) M. Shi and Y.-M. Xu, *Eur. J. Org. Chem.*, 2002, 696–701; (*c*) M. Shi, Y.-M. Xu, G.-L. Zhao and X.-F. Wu, *Eur. J. Org. Chem.*, 2002, 3666–3679; (*d*) M. Shi and Y.-M. Xu, *J. Org. Chem.*, 2003, **68**, 4784–4790; (*e*) G. L. Zhao, J.-W. Huang and M. Shi, *Org. Lett.*, 2003, **5**, 4737–4739.

4 T. G. Back and S. Collins, *J. Org. Chem.*, 1981, **46**, 3249–3256.

5 (*a*) T. G. Back and S. Collins, *Tetrahedron Lett.*, 1980, **21**, 2215–2218; (*b*) T. G. Back and S. Collins, *J. Org. Chem.*, 1981, **46**, 3249–3256; (*c*) R. A. Gancarz and J. L. Kice, *J. Org. Chem.*, 1981, **46**, 4899–4960; (*d*) Y.-H. Kang and J. L. Kice, *J. Org. Chem.*, 1984, **49**, 1507–1511; (*e*) T. G. Back, S. Collins and R. G. Kerr, *J. Org. Chem.*, 1983, **48**, 3077–3084; (*f*) T. G. Back, S. Collins, U. Gokhale and K.-W. Law, *J. Org. Chem.*, 1983, **48**, 4776–4779; (*g*) T. Miura and M. Kobayashi, *Chem. Commun.*, 1982, 438–439; (*h*) J. L. Kice and Y.-H. Kang, *Tetrahedron*, 1985, **41**, 4739–4746; (*i*) D. H. R. Barton, M. A. Csiba and J. C. Jaszberenyi, *Tetrahedron Lett.*, 1994, **35**, 2869–2872.

6 (*a*) T. G. Back, K. Brunner, M. V. Krishna, E. K. Y. Lai, and K. R. Muralidharan, in *Heteroatom Chemistry*, ed. E. Block, VCH, New York, 1990, Ch. 4; (*b*) T. G. Back, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1992, **67**, 203–218; (*c*) F. M. Leon and J. C. Carretero, *Tetrahedron. Lett.*, 1991, **32**, 5405–5408; (*d*) K. Hayakawa, M. Yodo, S. Ohsuki and K. Kanematsu, *J. Am. Chem. Soc.*, 1984, **106**, 6735–6740; (*e*) D. B. Reddy, N. C. Babu, V. Padmavathi and R. P. Sumathi, *Synthesis*, 1999, 491–494; (*f*) E. P. Kohler and R. G. Larsen, *J. Am. Chem. Soc.*, 1935, **57**, 1448–1452; (*g*) C. Najera, B. Baldo and M. Yus, *Chem. Commun.*, 1987, 92–94; (*h*) B. M. Trost, P. Seoane, S. Mignani and M. Acemoglu, *J. Am. Chem. Soc.*, 1989, **111**, 7487–7500.

7 (*a*) S. Alumni and W. P. Jencks, *J. Am. Chem. Soc.*, 1980, **102**, 2052–2060; (*b*) J. A. Linn, E. W. McLean and J. L. Kelly, *Chem. Commun.*, 1994, 913–914; (*c*) Y. Matsuya, K. Hayashi and H. Nemoto, *J. Am. Chem. Soc.*, 2003, **125**, 646–647; (*d*) W.-C. Shieh, S. Dell, A. Back, O. Repič and T. J. Blacklock, *J. Org. Chem.*, 2003, **68**, 1954–1957; (*e*) C. D. Pagageorgiou, S. V. Ley and M. J. Guant, *Angew. Chem., Int. Ed.*, 2003, **42**, 828–831; (*f*) N. Bremeyer, S. C. Smith, S. V. Ley and M. J. Guant, *Angew. Chem., Int. Ed.*, 2004, **43**, 2681–2684.