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Ethyl (benzothiazol-2-ylsulfonyl)acetate: a new reagent for the stereoselective synthesis of *α*,*β*-unsaturated esters from aldehydes†‡

Paul R. Blakemore,*§ Danny K. H. Ho and W. Mieke Nap
School of Chemistry, University of Leeds, Leeds, West Yorkshire, UK LS2 9JT.
E-mail: paul.blakemore@science.oregonstate.edu

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The title reagent engaged in the modified Julia olefination with aldehydes under mild reaction conditions (DBU, CH_2Cl_2, rt or −78 °C) to yield *α*,*β*-unsaturated esters; aryl aldehydes and aliphatic aldehydes possessing significant chain branching elements gave *trans* alkene products with high stereoselectivity (*E* : *Z* up to >98 : 2), while straight chain aliphatic aldehydes gave *cis* products preferentially (*Z* : *E* up to 92 : 8).

The *α*,*β*-unsaturated ester moiety boasts a rich chemistry and this useful structural unit is a common target of synthesis. Carbonyl olefination reactions, being inherently convergent and often highly stereoselective, offer an attractive route to conjugated enoates.[1] Of these methods, the Horner–Wadsworth–Emmons (HWE) reaction of phosphonoacetate derivatives is arguably the most versatile.[2] Herein, we report that the modified Julia olefination (one-pot Julia olefination) employing the title sulfonylacetate reagent offers a viable alternative to the HWE reaction for the stereoselective synthesis of simple *α*,*β*-unsaturated esters from aldehydes.

The modified Julia olefination, a direct synthesis of alkenes *via* the condensation of certain heteroaryl/aryl sulfonyl anions **2** with carbonyl compounds, has emerged as a useful tool for fragment linkage (Fig. 1).[3,4] This process was originally described with benzothiazol-2-yl (BT) sulfones[5] but has since been extended to include other types of heteroaryl sulfones (*e.g.* pyrid-2-yl (PYR),[5b,6] 1-phenyl-1*H*-tetrazol-5-yl (PT),[7] and 1-*tert*-butyl-1*H*-tetrazol-5-yl (TBT)[8] sulfones) and more recently non-heteroaryl 3,5-bis(trifluoromethyl)phenyl (BTFP)[9] sulfones.[10]

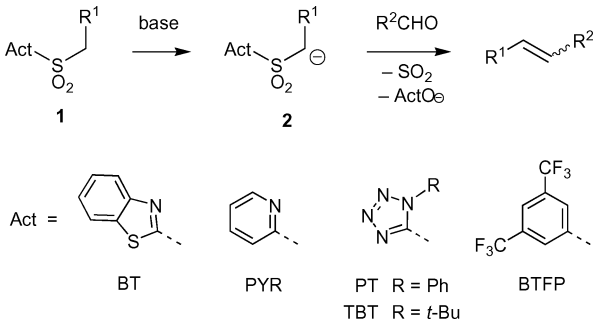
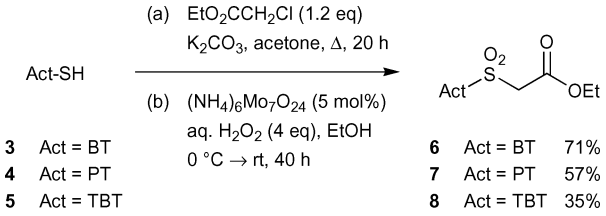


Fig. 1 The modified Julia olefination and common aromatic activators (Act): BT = benzothiazol-2-yl, PYR = pyrid-2-yl, PT = 1-phenyl-1*H*-tetrazol-5-yl, TBT = 1-*tert*-butyl-1*H*-tetrazol-5-yl, BTFP = 3,5-bis(trifluoromethyl)phenyl.

Substrate substituent effects are a major determinant of stereochemical outcome for the modified Julia olefination.[3] For example, BT-sulfonyl anions **2** which are semi-stabilized (R^1 = Ph, vinyl) generally react with straight-chain aliphatic aldehydes to afford (*Z*)-alkene products preferentially.[4a,b,5b] This bias for the *cis* olefin is heightened with analogous TBT-sulfones but may be reversed with PT-sulfones.[8] By contrast, branched aliphatic and aromatic aldehydes often give (*E*)-alkenes preferentially with all types of semi-stabilized heteroaryl sulfonyl anions **2**. Intrigued by whether similar behaviour would be exhibited by fully stabilized heteroaryl sulfonyl anions **2** (R^1 = carbonyl), and cognizant of the fact that the modified Julia olefination had not previously been applied to the synthesis of *α*,*β*-unsaturated esters, we duly prepared sulfones **6**–**8** and set about exploring their reactions with aldehydes.

BT-sulfone **6** was available in 71% overall yield (after recrystallization) from inexpensive 2-mercaptobenzothiazole (**3**) by base mediated *S*-alkylation with ethyl chloroacetate followed by ammonium molybdate catalyzed oxidation with hydrogen peroxide (Scheme 1).[11] PT- and TBT-sulfones **7** and **8** were similarly prepared, albeit in lower yield.[12] With this selection of sulfonyl acetates in hand, the synthesis of ethyl cinnamate (**9**) from benzaldehyde *via* modified Julia olefination was pursued in order to identify optimal reaction conditions (Table 1).



Scheme 1 Synthesis of heteroaryl sulfonyl acetates **6**–**8**.

Under conditions previously employed for the modified Julia olefination (NaHMDS, THF, −78 °C → rt), BT-sulfone **6** failed to react with benzaldehyde to any significant extent. This negative result was not surprising given that the stabilized enolate derived from **6** was expected to be a poor nucleophile. Nucleophilic competancy was conferred on the anion of **6** by briefly heating the reaction mixture to reflux. In this manner, *trans*-ethyl cinnamate (*E* : *Z* > 98 : 2) was produced in 63% yield based on benzaldehyde as the limiting reagent (entry 1). Disappointingly, little (if any) reaction was observed for tetrazolyl sulfones **7** and **8** under the same conditions (entries 2, 3)[13] and subsequent experiments were conducted with BT-sulfone **6**. Weaker ionic bases were next examined and both potassium *tert*-butoxide and cesium carbonate gave a modest yield of alkene product, although heating was again necessary (entries 4, 5). In an effort to identify milder conditions that might permit olefination at ambient temperature, the reaction was attempted with a series of neutral amine bases in tetrahydrofuran (entries 7 to 10). Triethylamine and 1,4-diazabicyclo[2.2.2]octane (DABCO) failed to promote olefination, but a combination of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and anhydrous

† Dedicated to the memory of Prof. Sylvestre A. Julia.

‡ Electronic supplementary information (ESI) available: experimental procedures and characterisation data for compounds **7** and **8**, spectral data (IR, ^{1}H NMR, ^{13}C NMR) for alkene products. See http://www.rsc.org/suppdata/ob/b5/b500713e/

§ Present address: Department of Chemistry, Oregon State University, 153 Gilbert Hall, Corvallis, Oregon 97331-4003, USA.

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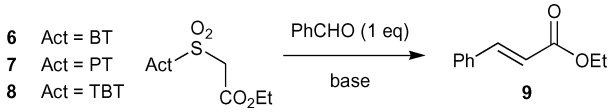
Table 1 Synthesis of ethyl (*E*)-cinnamate (**9**) by modified Julia olefination with heteroaryl sulfonyl acetates **6**–**8**



Entry	Sulfone (1.5 eq.)	Base (1.5 eq.)	Solvent	Temperature/°C	Time/h	Yield (%)[a]
1[b]	**6**	NaHMDS	THF	65	2	63
2[b]	**7**	NaHMDS	THF	65	2	5
3[b]	**8**	NaHMDS	THF	65	2	0
4	**6**	t-BuOK	THF	65	16	30
5	**6**	Cs_2CO_3	THF	65	24	31
6	**6**	None	THF	65	16	0
7	**6**	Et_3N	THF	23	70	0
8	**6**	DABCO	THF	23	16	0
9	**6**	DBU–LiCl	THF	23	20	21
10	**6**	DBU	THF	23	24	45
11[c]	**6**	DBU	MeOH	23	16	57
12	**6**	DBU	EtOH	23	16	66
13	**6**	DBU	MeCN	23	16	68
14	**6**	DBU	Et_2O	23	16	54
15	**6**	DBU	CH_2Cl_2	23	16	61
16[d]	**6**	DBU	CH_2Cl_2	23	16	78
17[e]	**6**	DBU	CH_2Cl_2	23	16	88

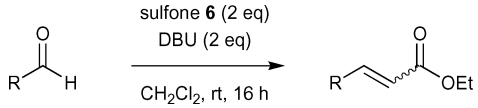
[a] ^{1}H NMR analysis indicated $E : Z \geq 95 : 5$ for all entries where **9** was produced. [b] NaHMDS (1.1 eq.) added to sulfone (1.2 eq.) at 0 °C, stirred for 30 min, then benzaldehyde added and heated to reflux for 2 h. [c] Reaction yielded methyl cinnamate. [d] Sulfone **6** (2 eq.)–DBU (2 eq.). [e] Sulfone **6** (3 eq.)–DBU (3 eq.).

lithium chloride, a reagent system introduced by Roush and Masamune for deprotonation of ketophosphonates in the HWE reaction,[14] gave 21% of **9** after 20 h at rt (entry 9). Pleasingly, the same experiment conducted without lithium chloride gave an improved yield of **9** in a comparable time period (entry 10).[15] With a mild and effective base identified, attention was directed at finding an optimum solvent for the Julia olefination between **6** and benzaldehyde (entries 11 to 15).[16] The reaction performed moderately well in all of the new media examined, including polar protic solvents, and in all cases, ethyl cinnamate was produced with $E : Z \geq 95{:}5$. Dichloromethane has favorable attributes for laboratory scale preparative chemistry (*e.g.* water immiscibility, low boiling point, low cost) and was chosen as the preferred solvent for further study. Acceptable yields of ethyl cinnamate (with $E : Z = 96 : 4$) were obtained within a convenient time frame by employing sulfone and base in two- or three-fold excess (entries 16, 17). Adopting the less extravagant of these two protocols, the wider scope of the olefination reaction with a range of different aldehydes was examined (Table 2).

Sulfone **6** olefinated aryl aldehydes in generally good yields using the standard reaction conditions (Table 2, entries 1 to 10). As expected from earlier results with benzaldehyde, (*E*)-configurated *α,β*-unsaturated esters were formed preferentially. Stereoselectivity was dependent on the steric demand of the aldehyde and its electronic character. Electron rich aryl aldehydes gave lower *trans* stereoselectivity than electron deficient examples (*e.g.* decreasing $E : Z$ from entry 1 to entry 4), while sterically congested aldehydes gave higher *trans* selectivity than comparable less encumbered examples (*cf.* entry 6 *vs.* entry 5; entry 9 *vs.* entry 8).

The reactions of sulfone **6** with a series of aliphatic aldehydes revealed interesting, though not entirely unexpected behaviour (entries 11 to 15). The stabilized anion of sulfone **6** reacted with *n*-hexanal to give a (*Z*)-enoate as the major product (entry 11).[17] Any preference for the *cis* isomer was, however, eroded upon incremental introduction of chain-branching elements onto the aldehyde substrate. Thus, citronellal, a representative *β*-branched aldehyde ($RC(Me)HCH_2CHO$), gave a significantly reduced $Z : E$ ratio as compared to *n*-hexanal (entry 12). With cyclohexanecarboxaldehyde, an *α*-branched aldehyde, the stereochemical bias was reversed in favor of the *trans* enoate (entry 13). Aliphatic aldehydes possessing greater steric encumbrance gave *trans* alkenes as the only detectable products (entries 14, 15). Olefination yield within the aliphatic series increased to a maximum for 2-ethylbutanal (entry 14), presumably a consequence of the greater stability of this hindered aldehyde (and the derived enoate product) to base mediated decomposition pathways. Pivalaldehyde, while also stable to decomposition, proved too hindered to react effectively with sulfone **7** and gave only 21% of alkene product (entry 15).

Table 2 Olefination of aromatic and alkyl aldehydes with ethyl (benzothiazol-2-ylsulfonyl)acetate (**6**)

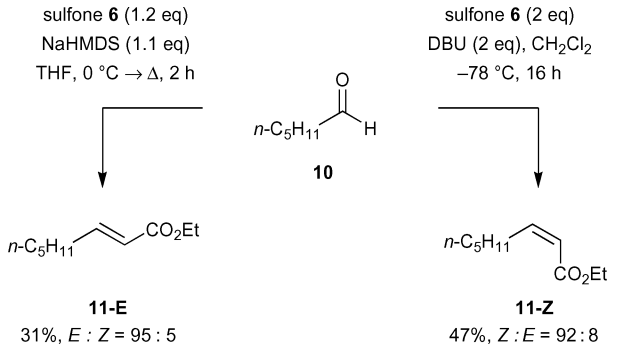


Entry	Aldehyde	Yield (%)	E : Z[a,b]
1	4-$(NO_2)C_6H_4CHO$	89	>98 : 2
2[c]	4-$(HO_2C)C_6H_4CHO$	57	96 : 4
3	4-ClC_6H_4CHO	77	95 : 5
4	4-$(MeO)C_6H_4CHO$	93	92 : 8
5	2-ClC_6H_4CHO	72	95 : 5
6	2,6-$Cl_2C_6H_3CHO$	83	>98 : 2
7	2,4,6-$Me_3C_6H_2CHO$	70	>98 : 2
8	2-Naphthaldehyde	65	93 : 7
9	1-Naphthaldehyde	86	96 : 4
10	Ferrocenecarboxaldehyde	82	96 : 4
11	*n*-$C_5H_{11}CHO$	41	19 : 81
12	Citronellal	64	30 : 70
13	*c*-$C_6H_{11}CHO$	80	80 : 20
14	Et_2CHCHO	88	>98 : 2
15	*t*-BuCHO	21	>98 : 2
16[d]	$PhCH_2CHO$	80	>98 : 2
17[e]	(*E*)-PhCH=CHCHO	—	N/a

[a] Determined by ^{1}H NMR analysis before chromatographic purification. [b] $E : Z > 98 : 2$ indicates only *trans*-isomer observable by ^{1}H NMR. [c] DBU (3 eq.). [d] Product was a mixture of *α,β*- and *β,γ*-unsaturated esters (1 : 9 respectively, both regioisomers $E : Z > 98 : 2$). [e] Reaction gave a complex mixture of intractable products.

The reactions of two miscellaneous carbonyl compounds with sulfone **6** revealed limitations to our method. Alkene formation from phenylacetaldehyde was non-regiospecific and the β,γ-unsaturated ester product predominated (entry 16). Attempted reaction with (*E*)-cinnamaldehyde, a representative α,β-unsaturated aldehyde, gave a complex mixture of intractable products (entry 17). Finally, it is worth noting that, acetophenone did not react with BT-sulfone **6** at all under two sets of reaction conditions tested (DBU, CH_2Cl_2, rt, or NaHMDS, THF, Δ).

The stereochemical outcomes of the reactions discussed above for sulfone **6** (Tables 1 and 2) are in accord with trends previously observed for semi-stabilized BT-sulfonyl anions (*vide supra*). At the outset of this study, we had hoped to develop a new synthesis of α,β-unsaturated esters which would allow for control of stereochemical preference by a simple choice of reaction conditions and/or activating group. Such programmability is possible in most cases with the HWE reaction.[18] The failure of tetrazolyl sulfones **7** and **8** to effectively olefinate aldehydes prevented us from achieving this goal by the exploitation of activator effects alone; however, in one case at least, we were able to demonstrate stereodivergent enoate formation by variation of reaction conditions (Scheme 2). Thus, treatment of *n*-hexanal (**10**) with BT-sulfone **6** and DBU in dichloromethane at −78 °C gave (*Z*)-oct-2-enoate **11**-*Z* with $Z : E = 92 : 8$, while (*E*)-oct-2-enoate **11**-*E* was formed preferentially from the same starting materials using NaHMDS as base in refluxing tetrahydrofuran.[19] It is anticipated that future advances along these lines will lead to a variant of the modified Julia olefination which will truly rival the HWE reaction for the programmable synthesis of (*E*)- or (*Z*)-configurated enoates.



Scheme 2 Stereodivergent synthesis of ethyl oct-2-enoate (**11**) from *n*-hexanal (**10**) by modified Julia olefination.

In summary, ethyl (benzothiazol-2-ylsulfonyl)acetate (**6**), a shelf-stable and easily handled crystalline solid,[20] has been demonstrated as a new reagent for the synthesis of α,β-unsaturated esters. Modified Julia olefination employing sulfone **6** occurred under mild reaction conditions (DBU, CH_2Cl_2, rt), required no special precautions (rigorous exclusion of air and moisture unnecessary), and gave excellent yields of *trans* enoate products for aromatic and moderately hindered aliphatic aldehydes. Non-hindered aliphatic aldehydes gave low to moderate yields of either (*E*)- or (*Z*)-enoate products depending on the reaction conditions.

Experimental

For a description of general techniques, details for the synthesis of sulfones **7** and **8**, and characterization data for all other compounds, refer to the electronic supplementary information.

Ethyl (benzothiazol-2-ylsulfonyl)acetate (6)

A stirred suspension of 2-mercaptobenzothiazole (**3**, 10.0 g, 59.8 mmol) and K_2CO_3 (9.9 g, 72 mmol) in acetone (100 mL) was treated with neat ethyl chloroacetate (7.6 mL, $d = 1.16$, 8.8 g, 72 mmol). The mixture was heated at reflux for 20 h, allowed to cool and filtered. Concentration of the filtrate *in vacuo* yielded 15.3 g of crude ethyl (benzothiazol-2-ylsulfanyl)acetate as a brown oil. A stirred solution of this material in EtOH (50 mL) at 0 °C was treated with $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (3.7 g, 3.0 mmol) followed by aq. H_2O_2 (23.1 mL, $d = 1.18$, 27.2 g, 30 wt%, 240 mmol). The resulting solution was allowed to warm slowly to rt and stirred for 42 h. After this time, the bulk of the EtOH solvent was removed *in vacuo* and the residue partitioned between EtOAc (50 mL) and H_2O (50 mL). The layers were separated and the aqueous phase extracted with EtOAc (2 × 25 mL). The combined organic extracts were washed with brine (20 mL), dried (Na_2SO_4) and concentrated *in vacuo* to yield 16.1 g of sulfone **6** as an off-white solid (>90% purity as adjudged by ^{1}H NMR analysis). Recrystallisation from *tert*-butyl methyl ether (TBME) afforded analytically pure ethyl (benzothiazol-2-ylsulfonyl)acetate (**6**, 12.1 g, 42.4 mmol, 71%) as colourless prisms: mp 58–59 °C (TBME) [lit.[11] mp 61–62 °C); IR (neat) 3461, 2983, 1736, 1470, 1273, 1152, 1026, 910, 853, 770, 614 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (1H, dd, $J = 7.1$, 1.8 Hz), 8.04 (1H, dd, $J = 7.0$, 1.9 Hz), 7.67 (1H, td, $J = 7.2$, 1.6 Hz), 7.62 (1H, td, $J = 7.3$, 1.6 Hz), 4.58 (2H, s), 4.18 (2H, q, $J = 7.2$ Hz), 1.17 (3H, t, $J = 7.1$ Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.0 (0), 161.7 (0), 152.5 (0), 137.1 (0), 128.4 (1), 127.9 (1), 125.7 (1), 122.5 (1), 62.9 (2), 58.9 (2), 13.9 (3) ppm; MS (ES+) m/z 286 $(M + H)^+$; Anal. Calcd. for $C_{11}H_{11}NO_4S_2$: C, 46.30; H, 3.89; N, 4.91. Found: C, 46.40; H, 4.00; N, 4.95.

General olefination procedure using DBU in CH_2Cl_2

A solution of BT-sulfone **6** (228 mg, 0.80 mmol) in CH_2Cl_2 (5 mL) was treated with DBU (0.12 mL, $d = 1.02$, 122 mg, 0.80 mmol) followed by the neat aldehyde (0.40 mmol) and stirred at rt for 16 h. After this time, saturated aqueous NH_4Cl (5 mL) was added and the layers shaken and separated. The aqueous phase was extracted (2 × 10 mL, CH_2Cl_2) and the combined organic phases were washed with brine (10 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, eluting with 5–20% EtOAc in hexanes) to yield the α,β-unsaturated ester product.

General olefination procedure using NaHMDS in THF

A stirred solution of BT-sulfone **6** (342 mg, 1.20 mmol) in anhydrous THF (10 mL) at 0 °C under N_2 was treated dropwise with NaHMDS (1.10 mL, 1.0 M in THF, 1.10 mmol). After stirring at 0 °C for 30 min, neat aldehyde (1.0 mmol) was added and the reaction mixture heated at reflux for 2 h. The mixture was then allowed to cool and partitioned between sat. aq. NH_4Cl (15 mL) and EtOAc (15 mL). The layers were separated and the aqueous phase was extracted with EtOAc (2 × 15 mL). The combined organic extracts were washed with brine (15 mL), dried (Na_2SO_4), and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, eluting with 5–20% EtOAc in hexanes) to yield the α,β-unsaturated ester product.

Acknowledgements

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10 Any aromatic moiety which can support *ipso* substitution of a sulfinate nucleofuge can potentially be used as an activating group in the modified Julia olefination.

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13 In each of these two experiments, >85% of tetrazolyl sulfone starting materials were recovered, indicating that failure of the reactions was not due to decomposition of the metalated sulfones.

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16 From this stage forward, all experiments were conducted with GPR grade solvents used as received, and no attempt was made to exclude air or adventitious moisture from reaction vessels.

17 In an attempt to increase *cis* selectivity in this case, the analogous reaction with TBT-sulfone **8** was conducted; however, the tetrazolyl sulfone again proved unreactive and was recovered in quantitative yield. Subsequently, the desired increase in stereoselectivity was achieved by conducting the coupling reaction of BT-sulfone **6** with *n*-hexanal at −78 °C (see Scheme 2).

18 The traditional HWE reaction employing diethylphosphonoacetates is generally (*E*)-selective (see ref. 2); however, bis(trifluoroethyl)- and diarylphosphonoacetates give (*Z*)-configurated enoates preferentially under appropriate reaction conditions, see: (*a*) W. C. Still and C. Gennari, *Tetrahedron Lett.*, 1983, **24**, 4405; (*b*) K. Ando, *Tetrahedron Lett.*, 1995, **36**, 4105; (*c*) K. Ando, T. Oishi, M. Hirama, H. Ohno and T. Ibuka, *J. Org. Chem.*, 2000, **65**, 4745.

19 That (*E*)-stereoselectivity in this case was not simply the result of base induced alkene isomerization was established as follows: Julia olefination of benzaldehyde by BT-sulfone **6** was carried out as previously described (Table 1, entry 1) in the presence methyl oct-2-enoate with $E : Z = 1 : 4$. Following work-up, and purification by column chromatography, the expected ethyl cinnamate product was obtained in 58% yield (with $E : Z > 98 : 2$) together with 78% of recovered methyl oct-2-enoate with $E : Z = 1 : 4$.

20 A colorless sample of crystalline sulfone **6** (mp 58–59 °C, TBME) darkened significantly during 12 months of storage in a screw-capped clear glass jar. Despite this discoloration, the aged sulfone exhibited no obvious signs of decomposition by ^{1}H NMR analysis and gave identical results in its olefination reactions with aldehydes as compared to those conducted with freshly prepared material.