DOI: 10.1002/ejoc.200600478

3,5-Bis(trifluoromethyl)phenyl Sulfones in the Julia–Kocienski Olefination – Application to the Synthesis of Tri- and Tetrasubstituted Olefins

Diego A. Alonso,[a] Mónica Fuensanta,[a] and Carmen Nájera*[a]

Keywords: Alkenes / Carbanions / Olefination / Sulfones / Phosphazenes

3,5-Bis(trifluoromethyl)phenyl (BTFP) sulfones **8a–d** are successfully employed in the modified Julia olefination reaction with carbonyl compounds employing phosphazene base P4-*t*Bu at room temp. in THF, affording tri- and tetrasubstituted olefins in good yields. The Julia–Kocienski olefination between primary alkyl BTFP sulfones **8a**,**b** and aromatic and aliphatic ketones affords the corresponding trisubstituted alkenes in good yields and low stereoselectivities. On the other hand, higher yields and stereoselectivities are obtained in the synthesis of trisubstituted olefins through the other approach, the coupling of secondary alkyl BTFP sulfones **8c**,**d** with aliphatic, aromatic and α,β-unsaturated aldehydes. For the first time, tetrasubstituted olefins are synthesized by means of the Julia–Kocienski protocol when the isopropyl BTFP sulfone **8c** reacts with aliphatic and aromatic ketones, employing P4-*t*Bu as base at THF reflux.
(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2006)

Introduction

The stereoselective synthesis of tri- and tetrasubstituted olefins represents one of the long-standing challenges in organic chemistry. During several decades, a variety of approaches to the synthesis of olefins have been developed in an attempt to address regio- and stereochemical demands. The most generally applicable methods involve the direct olefination of carbonyl compounds,[1] as in the Wittig,[2] Horner,[3] Wadsworth–Emmons,[4] Peterson,[5] Johnson,[6] and classical (Marc) Julia[7] reactions. These methodologies have played important roles in the synthesis of natural products containing the (*E*)- or (*Z*)-alkene moiety. The classical Julia olefination, also known as the Julia–Lythgoe olefination, was developed nearly thirty years ago and is based on a reductive elimination process of β-alkoxy sulfones.[8] Since its discovery, it has become a crucial step in the synthesis of many natural products.[9] Trisubstituted alkenes have been prepared by the reductive elimination of β-hydroxy sulfones but, in general, the reverse reaction competes. The reverse reaction is favoured when the β-alkoxy sulfone adduct is sterically encumbered. The olefination of ketones to prepare trisubstituted alkenes employing Na/Hg affords moderate yields, unpredictable stereoselectivities and large amounts of retro-aldol products from the intermediate β-alkoxy sulfones. High yields and moderate stereoselectivities of trisubstituted alkenes are obtained by a modification of the Julia–Lythgoe olefination reaction, involving the in situ capture of the intermediate β-alkoxy sulfones with a suitable oxophilic electrophile and the employment of SmI_2/HMPA to promote, under neutral conditions, the reductive elimination at low temperatures.[10] A variant of the classical Julia reaction, the Julia–Kocienski olefination, also called modified or one-pot Julia olefination,[11,12] has recently emerged as a powerful tool for olefin synthesis. Since the initial study by Silvestre Julia and co-workers of the reaction of metallated benzothiazol-2-yl sulfones (BT sulfones, **1**) with carbonyl compounds,[11a] the versatility of these derivatives has been fully demonstrated through their application in the total synthesis of a large number of biologically active natural products[11c] such as rapamycin,[13] (+)-herboxidiene A,[14] (–)-[15] and (+)-lasonolide A,[16] rhizoxin D,[17] phorboxazole A[18] and B,[19] peridin,[20] (–)-colombiasin A,[21] and (–)-elisapterosin B.[21] In addition, BT sulfones have been used in the preparation of a wide variety of olefin moieties such as dienes,[22] trienes,[22b,22c] fluoroalkenes,[23] vinyl ethers,[24] exomethylene sugars,[25] and α,β-unsaturated esters.[26] Other heterocyclic derivatives, such as pyridin-2-yl (PYR, **2**),[22a,27] 1-phenyl-1*H*-tetrazol-5-yl (PT, **3**),[28] and 1-*tert*-butyl-1*H*-tetrazol-5-yl (TBT, **4**),[29] and most notably the benzothiazol-2-yl[30] and 1-phenyl-1*H*-tetrazol-5-yl[31] derivatives have also provided useful levels of stereoselectivity in the one-pot Julia olefination.

We have recently shown that the BTFP group **5** (Figure 1) is a strong electron-withdrawing group, and the corresponding BTFP sulfonyl group is an excellent nucleofuge in base-promoted β-elimination processes.[32–35] Thus, α-arylsulfonyl acetates **6** (Figure 2) are very soft nucleophiles under phase-transfer-catalyzed (PTC) conditions and have been used in the direct synthesis of *E* aconitates by an alkylation-elimination integrated process.[32] On the other hand,

[a] Departamento de Química Orgánica and Instituto de Síntesis Orgánica (ISO), Facultad de Ciencias, Universidad de Alicante, Apartado 99, 03080 Alicante, Spain
E-mail: cnajera@ua.es

 © 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

β-arylsulfonyl ethanol **7** (Figure 2), is an efficient protecting group for carboxylic acids, easily removed with aqueous $NaHCO_3$.[33] We have very recently reported the successful use of alkyl BTFP sulfones **8** (Figure 2) (R = H, alkyl, aryl) in the stereoselective synthesis of 1,1- and 1,2-disubstituted olefins through the Julia–Kocienski olefination of aliphatic and aromatic aldehydes and ketones under very simple reaction conditions with KOH and phosphazenes as bases.[34] The presence of the BTFP group, which can support *ipso* substitution of the sulfonate nucleofuge, was also demonstrated to be responsible for the different reactivity and reaction pathway observed in a one-pot Julia olefination involving a Smiles rearrangement[35] and spontaneous elimination of sulfur dioxide and the corresponding phenol derivative[36] (Scheme 1). Now, we report the evaluation and optimization of BTFP sulfones **8** as nucleophilic partners in the synthesis of tri- and tetrasubstituted alkenes through the Julia–Kocienski olefination of aldehydes and ketones.[37]

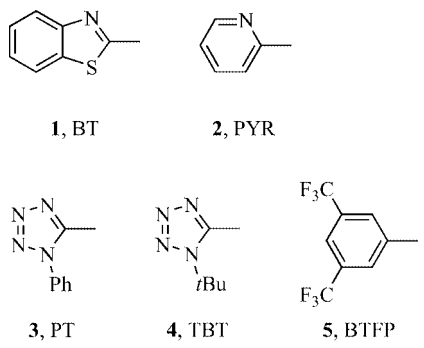


Figure 1. Heteroaryl and BTFP groups.

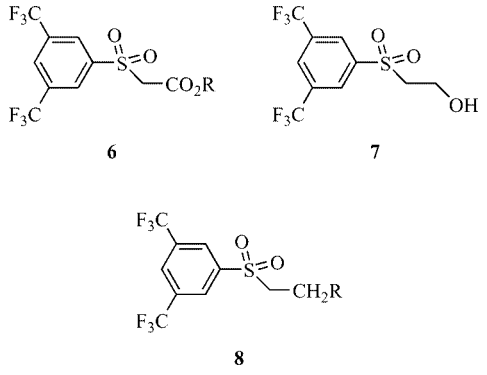
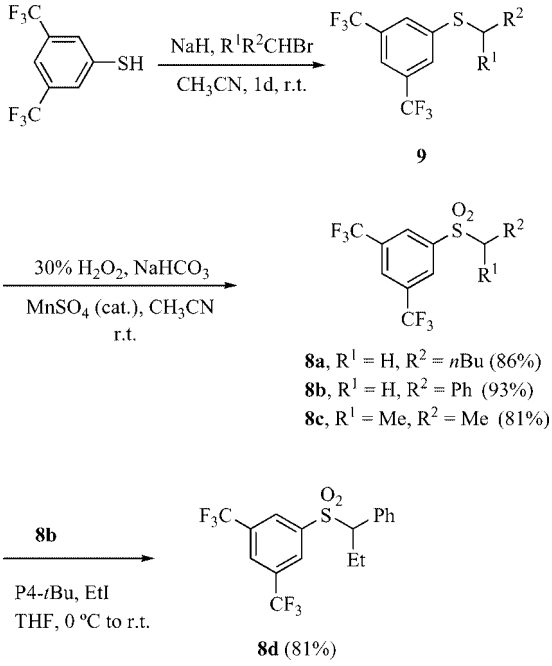


Figure 2. BTFP sulfonyl derivatives.

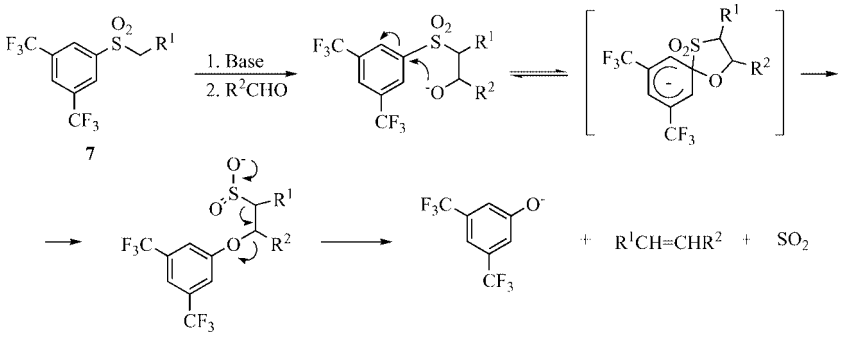
Results and Discussion

Different representative π-deficient BTFP sulfones **8a–d** were prepared in high yields by the reaction of 3,5-bis(trifluoromethyl)benzenethiol[38] with the corresponding alkyl bromide and NaH as base in CH_3CN at room temp. to afford sulfides **9** (Scheme 2). Thioethers **9** were oxidized without further purification to the sulfones **8a–c** with 30% H_2O_2 in the presence of catalytic amounts of $MnSO_4 \cdot H_2O$ (1 mol-%) and a buffer solution of $NaHCO_3$[39] (Scheme 2). Sulfone **8d** was synthesized in 81% yield from benzylic sulfone **8b** by deprotonation with phosphazene base P4-*t*Bu[40] and subsequent reaction with ethyl iodide (Scheme 2).



Scheme 2. Synthesis of BTFP sulfones **8a–d**.

Two different routes can be employed for the synthesis of trisubstituted olefins **10**—either olefination of aldehydes with secondary alkyl BTFP sulfones, such as the isopropyl analogue **8c** and the 1-phenyl-*n*-propyl analogue **8d**, or re-



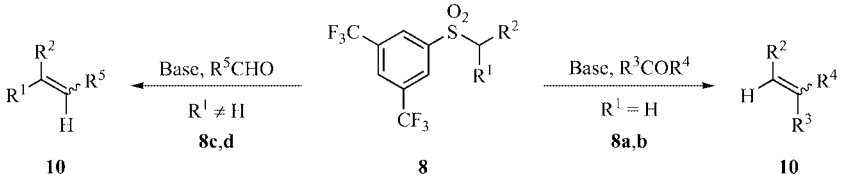
Scheme 1. Mechanism of the Julia–Kocienski olefination with BTFP sulfones.

 © 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

action between ketones and primary alkyl BTFP sulfones, such as the *n*-pentyl analogue **8a** and the benzyl analogue **8b** (Scheme 3, Table 1 and Table 2).

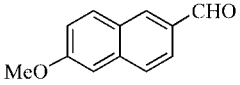
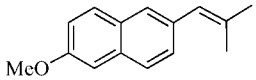
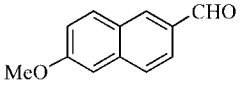
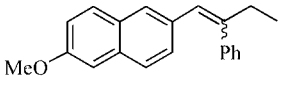
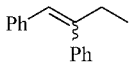
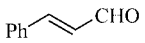
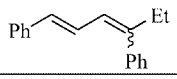
With respect to the olefination of aldehydes employing secondary alkyl sulfones **8c** and **8d**, a preliminary study was first conducted through the coupling between isopropyl BTFP sulfone **8c** and 6-methoxy-2-naphthaldehyde (Scheme 3, Table 1). The olefination was carried out, in all cases, under Barbier-type conditions (slow addition of the base to a mixture of the aldehyde and sulfone). Better yields were always observed for the olefination process under these conditions. We also observed better yields when an excess (2 equiv.) of sulfone was used. In this manner, the corresponding olefin was produced in a 71% yield, based on the ketone as the limiting reagent, when KOH was used as base in THF at room temp. (Table 1, compare entries 1 and 2). Metallated bases such as KHMDS gave very low yields (Table 1, entry 3). When the Schwesinger base BEMP was used, the reaction failed (Table 1, entry 4). However, the phosphazene P4-*t*Bu gave an excellent yield of alkene **10ca** at room temp. in THF (Table 1, entry 5). As shown in Table 1 (entries 2 and 5), the yield of the olefination reaction with KOH at room temp. was good (71%), though the best result was obtained with the Schwesinger base P4-*t*Bu at room temp. (95%). From these studies, it could be concluded that KOH was an appropriate base to carry out the Julia–Kocienski olefination between benzyl BTFP sulfone **8c** and aldehydes, even though higher yields were obtained with the phosphazene base P4-*t*Bu in THF at room temp.

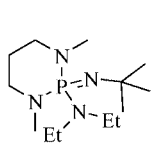
The olefination of different aromatic and aliphatic aldehydes with sulfones **8c** and **8d** was then performed according to the optimized conditions (Table 1, entries 6–13). BTFP sulfone **8c** olefinated aryl and alkyl aldehydes in generally good yields under the above-mentioned reaction con-



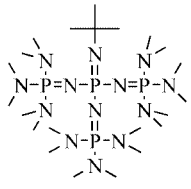
Scheme 3. Synthesis of trisubstituted olefins.

Table 1. Olefination of aldehydes with BTFP sulfones **8c**,**d**.[a]

Entry	BTFP **8** (equiv.)	R^3CHO	Base (equiv.)	T (°C)	Olefin **10** No.	Structure	Yield (%)[b]	Z/E[c]
1	**8c** (1)		KOH (9)[d]	r.t.	**10ca**		36	–
2	**8c** (2)		KOH (18)[d]	r.t.			71	–
3	**8c** (2)		KHMDS (2.4)	r.t.			<5	–
4	**8c** (2)		BEMP (2.4)	r.t.			<5	–
5	**8c** (2)		P4-*t*Bu (2.4)	r.t.			95	–
6	**8c** (2)	(*E*)-PhCH=CHCHO	P4-*t*Bu (2.4)	r.t.	**10cb**	(*E*)-PhCH=CHCH=$C(CH_3)_2$	89	–
7	**8c** (2)	$PhCH_2CH_2CHO$	P4-*t*Bu (2.4)	r.t.	**10cc**	$PhCH_2CH_2CH=C(CH_3)_2$	52	–
8	**8c** (2)	$nC_9H_{19}CHO$	P4-*t*Bu (2.4)	r.t.	**10cd**	$nC_9H_{19}CH=C(CH_3)_2$	67	–
9	**8d** (2)		P4-*t*Bu (2.4)	–78 to r.t.	**10da**		50	65/35
10	**8d** (2)	PhCHO	P4-*t*Bu (2.4)	–78 to r.t.	**10de**		77	70/30
11	**8d** (2)	PhCHO	P4-*t*Bu (2.4)	–78			50	85/15
12	**8d** (2)	PhCHO	P4-*t*Bu (2.4)[e]	–78			35	76/24
13	**8d** (2)		P4-*t*Bu (2.4)	–78 to r.t.	**10db**		63	93/7



BEMP

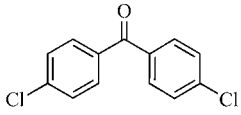
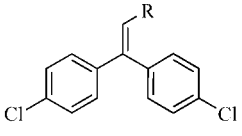
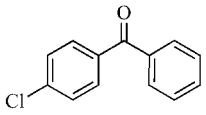
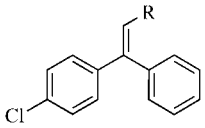
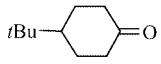
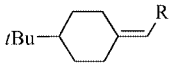
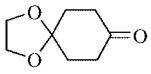
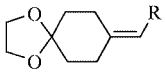
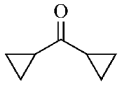
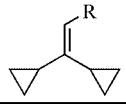


P4-*t*Bu

[a] The reactions were carried out in THF overnight and under Barbier conditions. [b] Isolated yield after flash chromatography. [c] Determined by ^1H NMR of the crude reaction mixture. [d] The reaction was carried out in the presence of 0.1 equiv. of TBAB. [e] The reaction was carried out in the presence of 2.4 equiv. of HMPA.

 © 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Table 2. Olefination of ketones with BTFP sulfones **8a**,**b**.[a]

Entry	BTFP **8** (equiv.)	R^2COR^3	Base (equiv.)	T (°C)	Olefin **10** No.	Structure	R	Yield (%)[b]
1	**8a** (1)		KOH (9)[c]	r.t.	**10af**		*n*Bu	16
2	**8a** (2)		Cs_2CO_3 (6)	70			*n*Bu	<5
3	**8a** (2)		CsOH (6)	70			*n*Bu	<5
4	**8a** (2)		CsOH (6)[d]	70			*n*Bu	<5
5	**8a** (2)		CsOH (6)[e]	70			*n*Bu	<5
6	**8a** (1)		P4-*t*Bu (2.4)	0 to r.t.			*n*Bu	97 (15)[f]
7	**8a** (2)		P4-*t*Bu (1.2)	0 to r.t.			*n*Bu	40
8	**8b** (2)		P4-*t*Bu (2.4)	0 to r.t.	**10bf**		Ph	<5
9	**8a** (2)	PhCOPh	P4-*t*Bu (2.4)	0 to r.t.	**10ag**	$(Ph)_2C{=}CHR$	*n*Bu	40
10	**8a** (3)		P4-*t*Bu (3.6)	0 to r.t.			*n*Bu	84
11	**8a** (2)		P4-*t*Bu (2.4)	0 to r.t.	**10ah**		*n*Bu	75[g]
12	**8a** (2)		P4-*t*Bu (2.4)	r.t. to reflux	**10ah**		*n*Bu	77[h]
13	**8a** (1)		P4-*t*Bu (1.2)	0 to r.t.	**10ai**		*n*Bu	16
14	**8a** (2)		P4-*t*Bu (2.4)	0 to r.t.			*n*Bu	60
15	**8b** (2)		P4-*t*Bu (2.4)	0 to r.t.	**10bi**		Ph	25
16	**8a** (1)		P4-*t*Bu (1.2)	0 to r.t.	**10aj**		*n*Bu	26
17	**8a** (2)		P4-*t*Bu (2.4)	0 to r.t.	**10aj**		*n*Bu	90
18	**8b** (2)		P4-*t*Bu (2.4)	0 to r.t.	**10bj**		Ph	90
19	**8a** (2)		P4-*t*Bu (2.4)	0 to r.t.	**10ak**		*n*Bu	35
20	**8b** (2)		P4-*t*Bu (2.4)	0 to r.t.	**10bk**		Ph	50[i]

[a] The reactions were carried out in THF overnight and under Barbier conditions. [b] Isolated yield after flash chromatography. [c] The reaction was carried out in the presence of 0.1 equiv. of TBAB. [d] CH_3CN was used as solvent. [e] THF/DMF (3:1) was used as solvent. [f] In brackets, isolated yield when Barbier conditions were not used. [g] (*Z*/*E*), 45:55, as determined by ^1H NMR of the crude reaction mixture. [h] (*Z*/*E*), 60:40, as determined by ^1H NMR of the crude reaction mixture. [i] Reaction conversion.

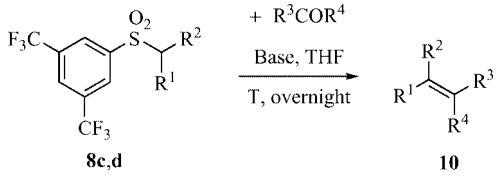
ditions. The olefination process was successful when coupling **8c** with (*E*)-cinnamaldehyde affording (*E*)-4-methyl-1-phenylpenta-1,3-diene (**10cb**) in an 89% yield (Table 1, entry 6). Regarding aliphatic aldehydes, isopropyl BTFP sulfone **8c** condensed with 3-phenylpropanal and decanal in the presence of phosphazene base P4-*t*Bu at room temp. (Table 1, entries 7 and 8) to give alkenes **10cc** and **10cd** in a 52% and 67% yield, respectively. Phosphazene base was also the most effective for the olefination of aldehydes with BTFP sulfone **8d** (Table 1, entries 9–14). Aromatic aldehydes such as 6-methoxy-2-naphthaldehyde and benzaldehyde yielded trisubstituted olefins **10da** and **10de**, respectively, in good yields and moderate stereoselectivities (Table 1, entries 9 and 10). In both cases, the reaction was (*Z*)-selective, and the selectivity, as shown for the case of benzaldehyde, could be improved by performing the reaction at low temperature (Table 1, entries 10 and 11). We have previously demonstrated the positive effect of certain additives such as HMPA on the stereoselectivity and yield of the olefination reaction of aromatic aldehydes with BTFP sulfones employing phosphazene base P4-*t*Bu.[34] However, this was not the case for the reaction between benzaldehyde and sulfone **8d**, which gave trisubstituted olefin **10de** with similar (*Z*) selectivity but in a lower 35% yield (Table 1, compare entries 10 and 12). Finally, a highly selective reaction took place between sulfone **8d** and (*E*)-cinnamaldehyde, affording (1*E*,3*Z*)-1,4-diphenylhexa-1,3-diene (**10db**) in a 63% yield (Table 1, entry 13).

A different approach to trisubstituted olefins consisted of the olefination of ketones with primary alkyl BTFP sulfones **8a** or **8b** (Scheme 3, Table 2). A preliminary base and solvent study was performed with sulfone **8a** and 4,4′-dichlorobenzophenone. A small screening showed the inefficiency of different inorganic bases such as KOH, Cs_2CO_3 and CsOH (Table 2, entries 1–5). The use of KOH in THF, which was efficient for the olefination of aldehydes with sulfone **8c** (see above) only gave a 16% yield of trisubstituted olefin **10af** (Table 2, entry 1). In the case of Cs_2CO_3, which has been used with little success in the olefination of aldehydes with activated BT-sulfonyl acetates,[26] the olefination reaction failed. When CsOH was employed as a base in different solvents such as THF, CH_3CN, and mixtures of THF/DMF[29b] the olefination failed, even when performed under heating conditions (Table 2, entries 3–5). In contrast, the use of phosphazene P4-*t*Bu in THF gave the desired olefin **10af** in a 97% yield (Table 2, entry 6). As in the case

 © 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

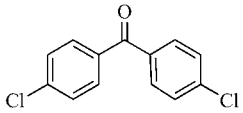
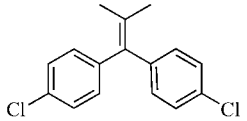
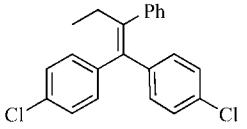
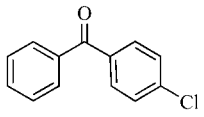
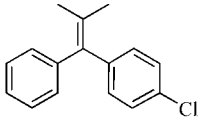
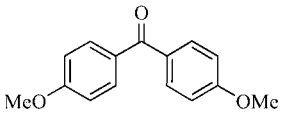
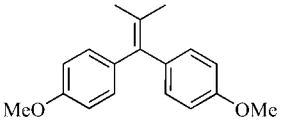
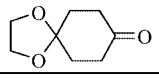
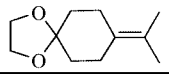
of the olefination of aldehydes with sulfones **8c** and **d**, it became rapidly clear that a Barbier-type procedure and an excess of the sulfone carbanion were most convenient, since much better yields were obtained under these conditions (Table 2, entries 6 and 7). Disappointingly, under the tested reaction conditions, benzyl BTFP sulfone **8b** failed to react with aromatic ketones to any significant extent (Table 2, entry 8).[41] This negative result was not surprising, given that the stabilized sulfone carbanion derived from **8b** was expected to be a poor nucleophile. Under the standard reaction conditions, pentyl BTFP sulfone **8a** reacted with benzophenone and 4-chlorobenzophenone in good yields to give the corresponding trisubstituted olefins **10ag** and **10ah**, respectively (Table 2, entries 9–12). As expected, in the latter case, the observed stereoselectivity was very low (Table 2, entries 11 and 12). On the other hand, good results were obtained for the olefination of aliphatic ketones with sulfone **8a** under the previously employed conditions (P4-*t*Bu, THF, 0° to room temp.) (Table 2, entries 14, 17, and 19). Thus 4-*tert*-butylcyclohexanone and pentyl sulfone **8a** gave alkene **10ai** in 60% yield (Table 2, entry 14). However, the coupling with the benzyl sulfone **8b** afforded alkene **10bi** in only 25% yield (Table 2, entry 15). Concerning the coupling with cyclohexa-1,4-dione monoethylene acetal, both sulfones reacted to give alkenes **10aj** and **10bj** in 90% yield (Table 2, entries 17 and 18). Again, the employment of a two-fold excess of nucleophile was necessary to obtain good yields (Table 2, compare entry 13 to entry 14 and entry 16 to entry 17). Finally, dicyclopropyl ketone gave alkenes **10ak** and **10bk** in moderate yields (Table 2, entries 19 and 20).

With regard to the synthesis of tetrasubstituted olefins, BTFP sulfone **8c** was first assayed under different reaction conditions as the olefination reagent for 4,4′-dichlorobenzophenone (Scheme 4 and Table 3). It turned out that, under Barbier-type conditions, the phosphazene base P4-*t*Bu in THF was again the base of choice for the synthesis of tetrasubstituted olefins. Under these conditions, sulfone **8c** reacted with 4,4′-dichlorobenzophenone to provide alkene **10cf** in a 30% yield (Table 3, entry 4). No improvement in yield was detected when the amount of nucleophile was increased to a three-fold excess (Table 3, entry 5). The nucleophilic ability of the enolate derived from **8c** was increased by heating the reaction mixture at reflux. In this manner, olefin **10cf** was produced in a 71% yield (Table 3, entry 6).



Scheme 4. Olefination of ketones with BTFP sulfones **7c**,**d**.

Table 3. Olefination of ketones with BTFP sulfones **8c**,**d**.[a]

Entry	BTFP **7** (equiv.)	R^3COR^4	Base (equiv.)	*T* (°C)	Olefin **10** No.	Structure	Yield (%)[b]
1	**8c** (2)		KOH (9)	r.t.	**10cf**		<5
2	**8c** (2)		NaH (2)	0 to r.t.			<5
3	**8c** (2)		KHMDS (2.4)	0 to r.t.			<5
4	**8c** (2)		P4-*t*Bu (2.4)	0 to r.t.			30
5	**8c** (3)		P4-*t*Bu (3.6)	0 to r.t.			35
6	**8c** (2)		P4-*t*Bu (2.4)	r.t. to reflux			71
7	**8d** (2)		P4-*t*Bu (2.4)	r.t. to reflux	**10df**		<5
8	**8c** (3)	PhCOPh	P4-*t*Bu (3.6)	r.t. to reflux	**10cg**	$(Ph)_2C{=}CMe_2$	40
9	**8c** (2)		P4-*t*Bu (2.4)	r.t. to reflux	**10ch**		70
10	**8c** (2)		P4-*t*Bu (2.4)	r.t. to reflux	**10ci**		10
11	**8c** (2)		P4-*t*Bu (2.4)	r.t. to reflux	**10cj**		35

[a] The reactions were carried out in THF overnight and under Barbier conditions. [b] Isolated yield after flash chromatography.

 © 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Under these conditions, olefination of 4,4′-dichlorobenzophenone with sulfone **8d** failed to give a product in significant yield (Table 3, entry 7). This was probably due to the lower reactivity of the sterically hindered secondary α-sulfonyl carbanion.[41] Concerning the olefination of aromatic ketones with BTFP sulfone **8c**, the electronic nature of the substrate proved to be determinant, given that electron-rich benzophenones such as 4,4′-dimethoxybenzophenone gave a very poor yield. Thus, benzophenone gave 40% of alkene **10cg** and 4-chlorobenzophenone gave 70% of **10ch** (Table 3, entries 8 and 9). However, 4,4′-dimethoxybenzophenone provided alkene **10cl** in only 10% yield (Table 3, entry 10). Finally, the olefination reaction with BTFP sulfone **8c** was carried out with monoprotected 1,4-cyclohexane-1,4-dione, giving alkene **10cj** in a moderate 35% yield (Table 3, entry 11). This was probably due to volatilization problems with the reaction product since the conversion of the reaction was very high.

Conclusions

In conclusion, the BTFP sulfonyl group has been shown to be a very stable and excellent activator for the synthesis of tri- and, for the first time, tetrasubstituted olefins through the Julia–Kocienski olefination reaction under very simple reaction conditions. From the assayed bases, the phosphazene base P4-*t*Bu is the most appropriate base for this type of coupling. Very good yields of trisubstituted olefins have been obtained through the coupling of secondary alkyl sulfones **8c** and **8d** with aromatic, aliphatic and α,β-unsaturated aldehydes. With respect to the benzylic BTFP sulfone **8d**, the diastereoselectivity of the process was moderate for aromatic aldehydes but excellent in the case of α,β-unsaturated aldehydes, being in all cases *Z*-selective. Alternatively, primary alkyl sulfones can be coupled with phenones and aliphatic ketones for the preparation of trisubstituted alkenes under the same reaction conditions. Isopropyl sulfone **8c** was also a very efficient olefinating reagent for diaryl and dialkyl ketones at THF reflux, affording the corresponding tetrasubstituted olefins in moderate to good yields. Additional applications of BTPF sulfones in olefination and other reactions are currently under investigation.

Experimental Section

General: Melting points were obtained with a Reichert Thermovar apparatus and were not corrected. IR data were collected on a FTIR apparatus (Nicolet Impact 400D), and peaks are reported in cm^{-1}. Only the most structurally important IR peaks have been listed. NMR spectra were recorded with a Bruker AC-300 (300 MHz for H^1 NMR and 75 MHz for ^{13}C NMR) spectrometer with $CDCl_3$ as solvent and TMS as internal standard, unless otherwise noted; chemical shifts are given in δ (ppm) and coupling constants (J) in Hz. Low-resolution electron-impact (EI) mass spectra were obtained at 70 eV with Shimadzu QP-5000 and Agilent 5973 spectrometers; fragment ions (m/z) are given, with relative intensities (%) in parenthesis. HRMS were recorded with a Finnigan MAT 95S spectrometer. Analytical TLC was visualized with UV light at 254 nm or with $KMnO_4$. Thin-layer chromatography was carried out on TLC aluminium sheets with silica gel 60 F_{254} (Merck). For flash chromatography, silica gel 60 (0.040–0.063 mm) was employed. Reactions under inert atmosphere (argon) were performed in oven-dried glassware, sealed with a rubber septum, in anhydrous CH_3CN or THF.

Compounds **8a**,[34c] **8b**,[34c] **9a**,[34c] **9b**,[34c] **10af**,[42] **10ag**,[43] **10ai**,[10] **10ak**,[44] **10bi**,[45] **10bj**,[46] **10bk**,[47] **10ca**,[48] **10cd**,[49] **10cf**,[50] **10cg**,[50] **10cj**,[51] **10cl**,[50] and **10de**[52] have been described previously. Compounds **10cb** and **10cc**, which are commercially available, gave satisfactory spectroscopic and physical data. ^1H NMR assignment and (*E*/*Z*) ratio determination for compounds **10da** and **10db** were performed with the aid of NOESY experiments on the isomeric mixture obtained after column chromatography.

General Procedure for the Synthesis of 3,5-Bis(trifluoromethyl)-phenyl Sulfanes 9a–c: To a room temperature solution of 3,5-bis(trifluoromethyl)benzenethiol (835 μL, 5 mmol) and NaH (95%, 150 mg, 6 mmol) in CH_3CN (15 mL) under argon was added the corresponding alkyl bromide (5.5 mmol), and the reaction was stirred at this temperature for 1 d. After quenching with H_2O (20 mL), the mixture was extracted with EtOAc (2 × 20 mL). The combined organic layers were dried (Na_2SO_4) and concentrated to afford the corresponding BTFP sulfanes **9a**–**c**, which were used in the next step without further purification.

3,5-Bis(trifluoromethyl)phenyl Isopropyl Sulfane (9c): (1.23 g, 85% crude yield); Yellow oil. IR: $\tilde{\nu}$ = 3090, 2967, 2928, 2844, 1626, 1370, 1128, 1123 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.75 (s, 2 H, ArH), 7.67 (s, 1 H, ArH), 3.54 (sept, $^3J_{H,H}$ = 6.7 Hz, 1 H, CH), 1.36 (d, $^3J_{H,H}$ = 6.7 Hz, 6 H, 2 CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.0 (ArC), 132.1 (q, J_{C-F} = 34.1 Hz, 2 CCF_3), 129.8 (ArCH), 123.1 (q, J_{C-F} = 273.3 Hz, 2 CF_3), 119.7 (ArCH), 37.9 (CH), 22.7 (2 CH_3) ppm. MS: m/z (%) = 288 (55) $[M]^+$, 269 (24), 247 (10), 246 (100), 145 (14), 226 (17), 225 (18).

General Procedure for the Synthesis of 3,5-Bis(trifluoromethyl)-phenyl Sulfones 8a–c: To a room temp. stirred solution of the corresponding sulfide **9a**–**c** (1 mmol) and $MnSO_4$ monohydrate (2 mg, 1 mol-%) in CH_3CN (23 mL), was slowly added a previously prepared, 0 °C, aqueous mixture comprised of 30% H_2O_2 (5 mmol, 515 μL) and a buffer solution of $NaHCO_3$ (0.2 M, 17 mL). After stirring for 1 d, the reaction was quenched with a saturated aqueous solution of NaCl (30 mL), extracted with EtOAc (2 × 20 mL) and dried with anhydrous Na_2SO_4. Filtration and evaporation of the solvents afforded the corresponding crude sulfones **8a**–**c**, which were recrystallized from hexane.

Isopropyl 3,5-Bis(trifluoromethyl)phenyl Sulfone (8c): (304 mg, 95%); White solid; R_f(hexane/EtOAc, 2:1) = 0.77; m.p. 80–83 °C. IR: $\tilde{\nu}$ = 3091, 2989, 2937, 1621, 1363, 1286, 1136 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.35 (s, 2 H, ArH), 8.17 (s, 1 H, ArH), 3.28 (sept, $^3J_{H,H}$ = 6.8 Hz, 1 H, CH), 1.35 (d, $^3J_{H,H}$ = 6.9 Hz, 6 H, 2 CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.1 (ArC), 133.0 (q, J_{C-F} = 34.8 Hz, 2 CCF_3), 129.3, 127.3 (ArCH), 122.3 (q, J_{C-F} = 273.3 Hz, 2 CF_3), 55.8 (CH), 15.4 (2 CH_3) ppm. MS: m/z (%) = 320 (0.06) $[M]^+$, 301 (14), 279 (10), 213 (15), 149 (21), 43 (100), 41 (24). HRMS: calcd. for $C_{11}H_{10}F_6O_2S$ $[M^+]$ 320.0306, $[M^+ - F]$ 301.0322; found 301.0325.

Experimental Procedure for the Synthesis of 1-Phenyl Propyl 3,5-Bis(trifluoromethyl)phenyl Sulfone (8d): Under an argon atmosphere, to a 0 °C stirred solution of sulfone **8b** (368 mg, 1 mmol) in anhydrous THF (20 mL), was added dropwise the phosphazene base P4-*t*Bu (1 M solution in *n*-hexane, 1.1 mL, 1 mmol). The mix-

 © 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

ture was stirred for 30 min at the same temperature before the addition of ethyl iodide (80 μL, 1 mmol). The reaction mixture was stirred overnight at room temperature and quenched with a saturated solution of NH_4Cl (5 mL). The mixture was extracted with EtOAc (2 × 10 mL), and the organic phase was dried (Na_2SO_4), filtered and the solvent evaporated to afford crude sulfone **8d** which was purified by flash chromatography (hexane/EtOAc, 9:1) to yield pure **8d**, (320.6 mg, 81%). White solid; R_f(hexane/EtOAc, 2:1) = 0.64; m.p. 69–71 °C. IR: $\tilde{\nu}$ = 3094, 3064, 2962, 2926, 2872, 1634, 1610, 1357, 1285, 1141 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.99 (s, 1 H, ArH), 7.83 (s, 2 H, ArH), 7.33–7.23 (m, 3 H, ArH), 7.06 (d, $^3J_{H,H}$ = 7.0 Hz, 2 H, ArH), 3.99 (dd, $^3J_{H,H}$ = 11.4 Hz, 3.9, 1 H, SCH), 2.64–2.51 (2 m, 2 H, 2 CH_2), 2.29–2.13 (2 m, 2 H, 2 CH_2), 0.94 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.0 (ArC), 132.3 (q, J_{C-F} = 35.3 Hz, 2 *C*CF_3), 131.1 (ArC), 129.7, 129.4, 129.37, 128.8, 126.8 (ArCH), 122.2 (q, J_{C-F} = 272.2 Hz, 2 CF_3), 73.6 (CH), 20.3 (CH_2), 11.4 (CH_3) ppm. MS: *m*/*z* (%) = 396 (0.06) $[M]^+$, 119 (64), 91 (100). HRMS: calcd. for $C_{17}H_{14}F_6O_2S$ $[M^+]$ 396.0619, $[M^+ - F]$ 377.0635; found 377.0653.

Typical Procedure for the Julia–Kocienski Olefination of 4-Chlorobenzophenone with BTFP Sulfone 8c: Under a Barbier protocol, to a room temp. stirred solution of sulfone **8c** (96 mg, 0.3 mmol) and 4-chlorobenzophenone (32 mg, 0.15 mmol) in anhydrous THF (6 mL) under argon, was added dropwise the phosphazene base P4-*t*Bu (1 M solution in *n*-hexane, 393 μL, 0.36 mmol). After stirring the reaction overnight at reflux, the solvent was evaporated, H_2O (5 mL) was added, and the mixture was extracted with pentane (2 × 10 mL). The organic phase was dried (Na_2SO_4), filtered, and the solvent evaporated to afford the corresponding crude olefin, which was purified by flash chromatography to give pure alkene **10ah** as a mixture of isomers (31 mg, 75%).

(*Z*/*E*)-1-(4-Chlorophenyl)-1-phenyl-1-hexene (10ah): Colourless oil; R_f(hexane) = 0.56. IR: $\tilde{\nu}$ = 3017, 3058, 2959, 2924, 2849, 1599 cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ = 7.31–7.17 (m, 14 H, ArH), 7.10 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, ArH), 6.97 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, ArH), 6.09 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H, C=C*H*), 6.01 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H, C=C*H*), 2.20–2.07 (m, 4 H, 2 CH_2); 1.41–1.24 (m, 8 H, 4 CH_2), 0.91–0.87 (m, 6 H, 2 CH_3) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 142.4, 141.3, 140.3, 140.2, 139.8, 138.7, 132.6, 132.4 (ArC, *C*=CH), 131.3, 130.88, 130.81, 129.8, 128.4, 128.3, 128.2, 128.1, 127.1, 127.99, 126.92 (ArCH, C=*C*H), 32.0, 29.49, 29.48, 22.3 (CH_2), 13.9 (CH_3) ppm. MS: *m*/*z* (%) = 272 (1) $[M^+ + 2]$, 271 (11) $[M^+ + 1]$, 270 (54) $[M]^+$, 235 (16), 229 (32), 228 (17), 227 (100), 214 (29), 193 (13), 192 (52), 191 (35), 189 (18), 179 (20), 178 (16), 165 (18), 151 (11), 149 (25), 125 (10), 115 (31), 91 (17). HRMS: calcd. for $C_{18}H_{19}Cl$ $[M^+]$ 270.1175; found 270.1195.

8-Pentylidene-1,4-dioxaspiro[4.5]decane (10aj): Yellow oil; R_f(hexane/EtOAc, 2:1) = 0.69. IR: $\tilde{\nu}$ = 2956, 2920, 2884, 1453, 1375, 1375, 1285, 1135, 1086, 1026 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.14 (t, $^3J_{H,H}$ = 7.0 Hz, 1 H, C=C*H*), 3.96 (s, 4 H, 2 OCH_2), 2.27–2.19 (4 m, 14 H, 7 CH_2), 2.00–1.98 (4 m, 14 H, 7 CH_2), 1.68–1.63 (4 m, 14 H, 7 CH_2), 1.32–1.29 (4 m, 14 H, 7 CH_2), 0.88 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.4 (*C*=CH), 123.1 (C=*C*H), 109.1 (OCO), 64.2 (2 OCH_2), 36.3, 35.5, 33.5, 32.2, 27.0, 24.9, 22.2 (7 CH_2), 13.9 (2 CH_3) ppm. MS: *m*/*z* (%) = 210 (41) $[M]^+$, 181 (10), 167 (19), 153 (22), 109 (13), 99 (15), 87 (17), 86 (100). HRMS: calcd. for $C_{13}H_{22}O_2$ $[M^+]$ 210.1620; found 210.1587.

1-(4-Chlorophenyl)-1-methyl-2-phenyl-1-propene (10ch): Colourless oil; R_f(hexane) = 0.53. IR: $\tilde{\nu}$ = 3083, 3064, 3026, 2983, 2918, 2848, 1649, 1600, 1568, 1482, 1450, 1401, 1369 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.30–7.16 (2 m, 9 H, ArH), 7.11–7.03 (2 m, 9 H, ArH), 1.79 (s, 6 H, 2 CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.8, 141.6, 135.8, 131.7, 131.2, 129.8, 128.0, 127.9, 126.2 (C=C, ArCH), 22.5, 22.4 (CH_3) ppm. MS: *m*/*z* (%) = 244 (33) $[M^+ + 2]$, 271 (9) $[M^+ + 1]$, 242 (100) $[M]^+$, 227 (19), 207 (16), 192 (27), 191 (17), 189 (13), 178 (15), 165 (26), 129 (30), 115 (18), 91 (13). HRMS: calcd. for $C_{16}H_{15}Cl$ $[M^+]$ 242.0862; found 242.0871.

(*Z*/*E*)-6-Methoxy-2-(2-phenyl-1-butenyl)naphthalene (10da): Colourless oil; R_f(pentane) = 0.44. IR: $\tilde{\nu}$ = 3062, 2975, 2925, 2867 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.72 (d, $^3J_{H,H}$ = 8.6 Hz, 2 H, ArH), 7.52–7.19 (2 m, 20 H, ArH), 7.19–6.92 (2 m, 20 H, ArH), 6.81 [s, 1 H, (*E*)-*H*C=C], 6.55 [s, 1 H, (*Z*)-*H*C=C], 3.93 [s, 3 H, (*E*)-OCH_3], 3.86 [s, 3 H, (*Z*)-OCH_3], 2.81 [q, $^3J_{H,H}$ = 7.5 Hz, 2 H, (*E*)-CH_2], 2.55 [q, $^3J_{H,H}$ = 7.4 Hz, 2 H, (*Z*)-CH_2], 1.12 [t, $^3J_{H,H}$ = 7.5 Hz, 3 H, (*E*)-CH_3], 1.09 [t, $^3J_{H,H}$ = 7.4 Hz, 3 H, (*Z*)-CH_3] ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.6, 157.4, 144.5, 144.2, 142.7, 141.5, 133.6, 133.0, 132.9 (*C*=CH, ArC), 129.4, 129.3, 128.8, 128.7, 128.6, 128.4, 128.3, 127.7, 127.6, 127.1, 126.8, 126.6, 126.5, 125.8, 125.1, 118.9, 118.4, 105.6, 105.4 (C=*C*H, ArCH), 55.3, 55.2 (OCH_3), 30.3, 29.7 (CH_2), 12.9 (2 CH_3) ppm. MS: *m*/*z* (%) = 289 (23) $[M^+ + 1]$, 288 (100) $[M]^+$, 273 (26), 241 (12), 215 (11), 171 (11), 115 (11). HRMS: calcd. for $C_{21}H_{20}O$ $[M^+]$ 288.1514; found 288.1495.

(1*E*,3*Z*)-1,4-Diphenyl-1,3-hexadiene (10db): Colourless oil; R_f(pentane) = 0.25. IR: $\tilde{\nu}$ = 3076, 3058, 3022, 2962, 2914, 2854, 2892, 1598, 1501 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.34–7.04 (m, 10 H, ArH), 6.72 (dd, $^3J_{H,H}$ = 15.6 Hz, 10.8, 1 H, *H*C=CHPh), 6.47 (d, $^3J_{H,H}$ = 15.8 Hz, 1 H, C=C*H*Ph), 6.21 (d, $^3J_{H,H}$ = 10.9 Hz, 1 H, *H*C=CEtPh), 2.43 (q, $^3J_{H,H}$ = 7.3 Hz, 2 H, CH_2), 0.97 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.1, 140.8, 137.7 (HC=*C*EtPh, ArC), 131.3, 128.7, 128.4, 128.1, 127.0, 126.9, 126.7, 126.2, 125.8 (3 =CH, ArCH), 32.06 (CH_2), 13.05 (CH_3) ppm. MS: *m*/*z* (%) = 234 (34) $[M]^+$, 206 (18), 205 (100), 204 (13), 202 (14), 128 (11), 115 (15), 91 (18). HRMS: calcd. for $C_{18}H_{18}$ $[M^+]$ 234.1409; found 234.1419.

Acknowledgments

This work has been supported by the Dirección General de Investigación of the Ministerio de Educación y Ciencia (CTQ2004-00808/BQU), by the Generalitat Valenciana (CTIOIB/2002/320, GRUPOS03/134, GRUPOS05/11 and GV05/157) and the University of Alicante. M. F. thanks the University of Alicante for a predoctoral fellowship.

[1] a) T. Takeda, *Modern Carbonyl Olefination*, Wiley-VCH, Weinheim, **2004**; b) V. N. Korotchenko, V. G. Nenajdenko, E. S. Balenkova, A. V. Shastin, *Russ. Chem. Rev.* **2004**, *73*, 957–989.
[2] a) G. Wittig, G. Geissler, *Justus Liebigs Ann. Chem.* **1953**, *580*, 44–68; b) B. E. Maryanoff, A. B. Reitz, *Chem. Rev.* **1989**, *89*, 863–927.
[3] a) L. Horner, H. Hoffmann, H. C. Wipel, G. Klahre, *Chem. Ber.* **1959**, *92*, 2499–2505; b) J. Clayden, S. Warren, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 241–270.
[4] a) W. S. Wadsworth Jr, W. D. Emmons, *J. Am. Chem. Soc.* **1961**, *83*, 1733–1738; b) J. Boutagy, R. Thomas, *Chem. Rev.* **1974**, *74*, 87–89.
[5] a) D. J. Peterson, *J. Org. Chem.* **1968**, *33*, 780–784; b) L. F. van Staden, D. Gravestock, D. J. Ager, *Chem. Soc. Rev.* **2002**, *31*, 195–200.
[6] C. R. Johnson, J. R. Shanklin, R. A. Kirchhoff, *J. Am. Chem. Soc.* **1973**, *95*, 6462–6463.
[7] M. Julia, J.-M. Paris, *Tetrahedron Lett.* **1973**, *14*, 4833–4836.
[8] For a review on desulfonylation reactions, see: C. Nájera, M. Yus, *Tetrahedron* **1999**, *55*, 10547–10658.

 © 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

[9] E. N. Prilezhaeva, *Russ. Chem. Rev.* **2000**, *69*, 367–408.
[10] I. E. Markó, F. Murphy, L. Kumps, A. Ates, R. Touillaux, D. Craig, S. Carballares, S. Dolan, *Tetrahedron* **2001**, *57*, 2609–2619.
[11] a) J. B. Baudin, G. Hareau, S. A. Julia, O. Ruel, *Tetrahedron Lett.* **1991**, *32*, 1175–1178; b) J. B. Baudin, G. Hareau, S. A. Julia, R. Lorne, O. Ruel, *Bull. Soc. Chim. Fr.* **1993**, *130*, 336–357; c) J. B. Baudin, G. Hareau, S. A. Julia, R. Lorne, O. Ruel, *Bull. Soc. Chim. Fr.* **1993**, *130*, 856–878.
[12] For a recent review, see: P. R. Blakemore, *J. Chem. Soc., Perkin Trans. 1* **2002**, 2563–2585.
[13] R. Bellingham, K. Jarowicki, P. Kocienski, V. Martin, *Synthesis* **1996**, 285–296.
[14] P. Kocienski, *Synthesis* **1996**, 652–666.
[15] E. Lee, H. Y. Song, J. W. Kang, D.-S. Kim, C.-K. Jung, J. M. Joo, *J. Am. Chem. Soc.* **2002**, *124*, 384–385.
[16] a) S. H. Kang, S. Y. Kang, C. M. Kim, H.-W. Choi, H.-S. Jun, B. M. Lee, C. M. Park, J. W. Jeong, *Angew. Chem. Int. Ed.* **2003**, *42*, 4779–4782; b) S. H. Kang, S. Y. Kang, H.-W. Choi, C. M. Kim, H.-S. Jun, J.-H. Youn, *Synthesis* **2004**, 1102–1114.
[17] a) J. A. Lafontaine, D. P. Provencal, C. Gardelli, J. W. Leahy, *Tetrahedron Lett.* **1999**, *40*, 4145–4148; b) J. A. Lafontaine, D. P. Provencal, C. Gardelli, J. W. Leahy, *J. Org. Chem.* **2003**, *68*, 4215–4234; c) Y. Jiang, J. Hong, S. D. Burke, *Org. Lett.* **2004**, *6*, 1445–1448.
[18] a) G. Pattenden, A. T. Plowright, J. A. Tornos, T. Ye, *Tetrahedron Lett.* **1998**, *39*, 6099–6102; b) G. Pattenden, M. A. González, P. B. Little, D. S. Millan, A. T. Plowright, J. A. Tornos, T. Ye, *Org. Biomol. Chem.* **2003**, *1*, 4173–4208; c) G. Pattenden, M. A. González, *Angew. Chem. Int. Ed.* **2003**, *42*, 1255–1258.
[19] a) D. A. Evans, V. J. Cee, T. E. Smith, D. M. Fitch, P. S. Cho, *Angew. Chem. Int. Ed.* **2000**, *39*, 2533–2536; b) D. R. Li, Y. Q. Tu, G.-Q. Lin, W.-S. Zhou, *Tetrahedron Lett.* **2003**, *44*, 8729–8732; c) D. R. Li, C. Y. Sun, C. Su, G.-Q. Lin, W.-S. Zhou, *Org. Lett.* **2004**, *6*, 4261–4264.
[20] a) N. Furuichi, H. Hara, T. Osaki, M. Nakano, H. Mori, S. Katsumura, *J. Org. Chem.* **2004**, *69*, 7949–7959; b) B. Vaz, R. Alvarez, R. Brückner, A. R. de Lera, *Org. Lett.* **2005**, *7*, 545–548.
[21] D. C. Harrowven, D. D. Pascoe, D. Demurtas, H. O. Bourne, *Angew. Chem. Int. Ed.* **2005**, *44*, 1221–1222.
[22] a) A. B. Charette, C. Berthelette, D. St-Martin, *Tetrahedron Lett.* **2001**, *42*, 5149–5153; Corrigendum: A. B. Charette, C. Berthelette, D. St-Martin, *Tetrahedron Lett.* **2001**, *42*, 6619; b) A. Sorg, R. Brückner, *Synlett* **2005**, 289–293; c) B. Vaz, R. Alvarez, J. A. Souto, A. R. de Lera, *Synlett* **2005**, 294–298.
[23] D. Chevrie, T. Lequeux, J. P. Demoute, S. Pazenok, *Tetrahedron Lett.* **2003**, *44*, 8127–8130.
[24] S. Surprenant, W. Y. Chan, C. Berthelette, *Org. Lett.* **2003**, *5*, 4851–4854.
[25] D. Gueyrard, R. Haddoub, A. Salem, N. S. Bacar, P. G. Goekjian, *Synlett* **2005**, 520–522.
[26] P. R. Blakemore, D. K. H. Ho, W. M. Nap, *Org. Biomol. Chem.* **2005**, *3*, 1365–1368.
[27] P. Mauleón, J. C. Carretero, *Org. Lett.* **2004**, *6*, 3195–3198.
[28] a) P. R. Blakemore, W. J. Cole, P. J. Kocienski, A. Morley, *Synlett* **1998**, 26–28; b) P. Jankowski, K. Plesniak, J. Wicha, *Org. Lett.* **2003**, *5*, 2789–2792.
[29] a) P. J. Kocienski, A. Bell, P. R. Blakemore, *Synlett* **2000**, 365–366; b) C. Aïssa, *J. Org. Chem.* **2006**, *71*, 360–363.
[30] For the latest applications of PT-sulfones in total synthesis, see: a) C. Marti, E. M. Carreira, *J. Am. Chem. Soc.* **2005**, *127*, 11505–11515; b) S. Dandapani, M. Jeske, D. P. Curran, *J. Org. Chem.* **2005**, *70*, 9447–9462; c) M. F. Jacobsen, J. E. Moses, R. M. Adlington, J. E. Baldwin, *Tetrahedron* **2006**, *62*, 1675–1689; d) G. Toschi, M. S. Baird, *Tetrahedron* **2006**, *62*, 3221–3227; e) D.-R. Li, D.-H. Zhang, C.-Y. Sun, J.-W. Zhang, L. Yang, J. Chen, B. Liu, C. Su, W.-S. Zhou, G.-Q. Lin, *Chem. Eur. J.* **2006**, *12*, 1185–1204; f) H. Motoyoshi, M. Horigome, H. Watanabe, T. Kitahara, *Tetrahedron* **2006**, *62*, 1378–1389.
[31] For the latest applications of PT-sulfones in total synthesis, see: a) N. Cramer, S. Laschat, A. Baro, H. Schwalbe, C. Richter, *Angew. Chem. Int. Ed.* **2005**, *44*, 820–822; b) C. Jasper, R. Wittenberg, M. Quitschalle, J. Jakupovic, A. Kirschning, *Org. Lett.* **2005**, *7*, 479–482; c) X. Gao, D. G. Hall, *J. Am. Chem. Soc.* **2005**, *127*, 1628–1629; d) D. Bondar, J. Liu, T. Müller, L. A. Paquette, *Org. Lett.* **2005**, *7*, 1813–1816; e) M. J. Schnermann, D. L. Boger, *J. Am. Chem. Soc.* **2005**, *127*, 15704–15705; f) S. Hara, K. Makino, Y. Hamada, *Tetrahedron Lett.* **2006**, *47*, 1081–1085.
[32] a) D. A. Alonso, C. Nájera, M. Varea, *Tetrahedron Lett.* **2001**, *42*, 8845–8848; b) D. A. Alonso, C. Nájera, M. Varea, *Helv. Chim. Acta* **2002**, *85*, 4287–4305.
[33] D. A. Alonso, C. Nájera, M. Varea, *Synthesis* **2003**, 277–287.
[34] a) D. A. Alonso, C. Nájera, M. Varea, *Tetrahedron Lett.* **2004**, *45*, 573–577; b) D. A. Alonso, M. Fuensanta, C. Nájera, M. Varea, *Phosphorus Sulfur Silicon Relat. Elem.* **2005**, *180*, 1119–1131; c) D. A. Alonso, M. Fuensanta, C. Nájera, M. Varea, *J. Org. Chem.* **2005**, *70*, 6404–6416.
[35] W. E. Truce, E. M. Kreider, W. W. Brand, *Org. React.* **1970**, *18*, 99–215.
[36] Very recently, the application of 4-nitrophenyl sulfones in the modified Julia olefination of aldehydes has been reported: D. Mirk, J.-M. Grassot, J. Zhu, *Synlett* **2006**, 1255–1259.
[37] To the best of our knowledge, only one example has been recently reported on the synthesis of a trisubstituted olefin through a modified Julia olefination employing a secondary alkyl PT sulfone. See ref.[30a].
[38] D. A. Alonso, C. Nájera, in *Electronic Encyclopedia of Reagents for Organic Synthesis* (RN00619) (Ed.: L. A. Paquette), Wiley, **2005**.
[39] This is a simple, green and general method for the oxidation of sulfides to sulfones: D. A. Alonso, C. Nájera, M. Varea, *Tetrahedron Lett.* **2002**, *43*, 3459–3461.
[40] a) R. Schwesinger, *Encyclopedia of Reagents for Organic Synthesis* (Ed.: L. A. Paquette), Wiley, Chichester, **1995**; vol. 6, p. 4110; b) R. Schwesinger, H. Schlemper, C. Hasenfratz, J. Willaredt, T. Dambacher, T. Breuer, C. Ottaway, M. Fletschinger, J. Boele, H. Fritz, D. Putzas, H. W. Rotter, F. G. Bordwell, A. V. Satish, G.-Z. Ji, E. M. Peters, K. Peters, H. G. von Schnering, L. Walz, *Liebigs Ann.* **1996**, 1055–1081; c) D. Seebach, A. K. Beck, A. Studer, *Modern Synthetic Methods*, Sauerländer AG, Aarau, Switzerland, **1995**, vol. 7, 1–178.
[41] In this experiment, >90% of the starting BTFP sulfone **8d** was recovered, indicating that the failure of the reaction was not due to decomposition of the sulfone carbanion.
[42] I. Kerner, W. Klein, F. Korte, *Tetrahedron* **1972**, *28*, 1575–1578.
[43] C. Ha, J. H. Horner, M. Newcomb, T. R. Varick, B. R. Arnold, J. Lusztyk, *J. Org. Chem.* **1993**, *58*, 1194–1198.
[44] G. Koebrich, D. Merkel, *Angew. Chem. Int. Ed. Engl.* **1970**, *9*, 243–244.
[45] R. P. Polniaszek, A. L. Foster, *J. Org. Chem.* **1991**, *56*, 3137–3146.
[46] T. Satoh, K. Takana, H. Ota, H. Someya, K. Matsuda, M. Koyma, *Tetrahedron* **1998**, *54*, 5557–5574.
[47] V. Usieli, S. Sarel, *J. Org. Chem.* **1973**, *38*, 1703–1708.
[48] M. Yasuda, R. Kojima, R. Ohira, T. Shiragami, K. Shima, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1655–1660.
[49] H. Tanaka, K. Hashimoto, K. Suzuki, Y. Kitaichi, M. Sato, T. Ikeno, T. Yamada, *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1905–1914.
[50] J. H. Incremona, J. C. Martin, *J. Am. Chem. Soc.* **1970**, *92*, 627–634.
[51] G. Revial, I. Jabin, M. Pfau, *Tetrahedron: Asymmetry* **2000**, *11*, 4975–4983.
[52] G. Guanti, L. Banfi, R. Riva, *Tetrahedron* **1995**, *51*, 10343–10360.

Received: June 2, 2006
Published Online: August 15, 2006

 © 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim