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Olefination with sulfonyl halides and esters – sulfur-based variant of the Horner-Wadsworth-Emmons reaction

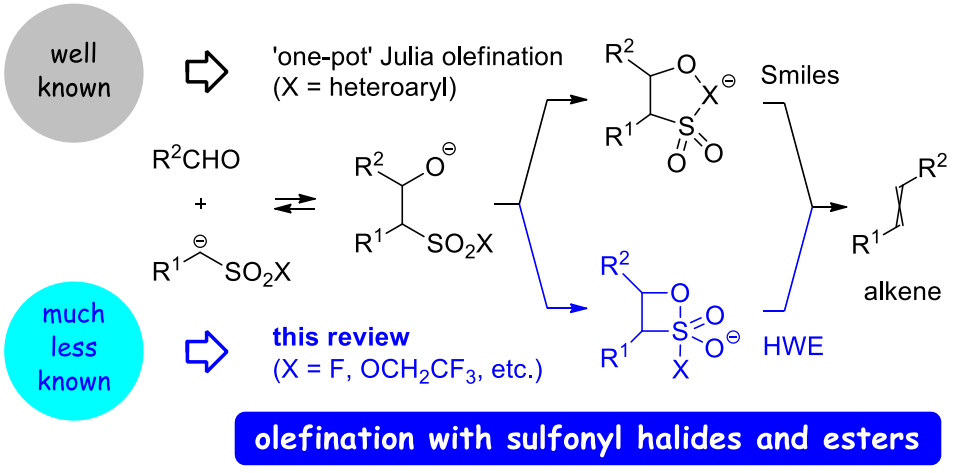
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Abstract

Among carbonyl olefination reactions sulfur-based protocols play a prominent role, utilizing aryl and hetaryl sulfones in processes referred as 'classical' and 'one-pot' Julia olefinations. However, a related, but much less common method, which is based on the reactivity of sulfonyl halides and esters (sulfonates), features a different reaction mechanism. Accordingly, carbanions of the precursors add to aldehydes and ketones, cyclize to four membered ring intermediates and *syn*-fragment to alkenes, mimicking transformations of organic phosphonates (the Horner-Wadsworth-Emmons reaction). The presented mini-review compiles early reports from the 1990s with a series of recent articles, in which the 'overlooked' olefination method was systematically studied.



Keywords: Alkenes, olefination, sulfonates, sulfonyl halides, carbanions, selectivity

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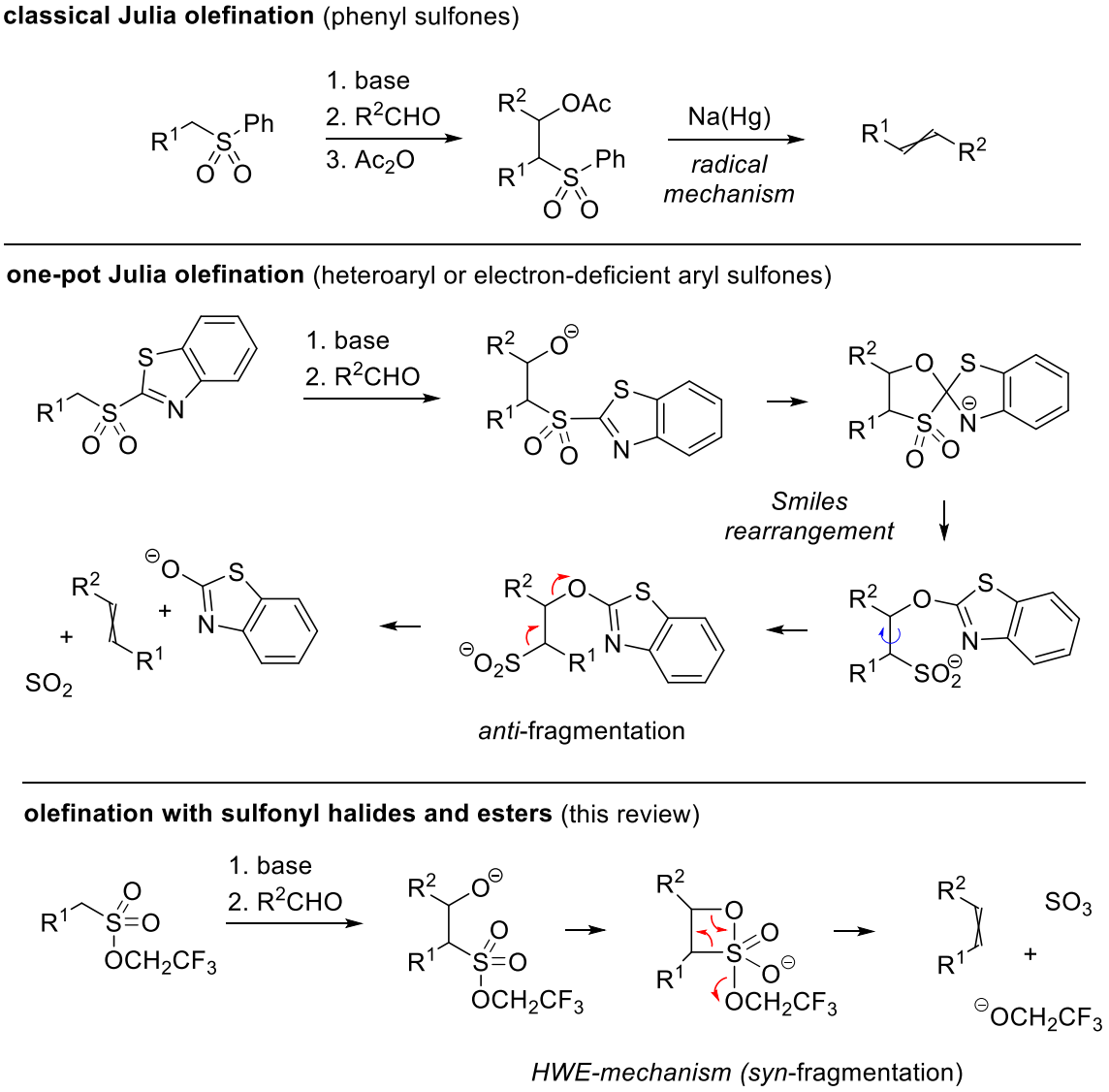
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1. Introduction

The formation of C=C bonds plays a crucial role in the field of organic synthesis. There are numerous methods of carbonyl group olefination utilizing derivatives of phosphorus,[1] sulfur[2,3] and silicon[4] described in the literature. In the case of sulfur-based reactions, the most known protocols are 'classical' Julia olefination (also known as the Julia-Lythgoe olefination) with alkyl phenyl sulfones, which requires a tedious three-step sequence of addition, acylation and reduction, and 'one-pot' Julia olefination (also known as the Julia-Kocienski olefination or the 'modified' Julia olefination) using hetaryl sulfones, which spontaneously transform carbonyl compounds to the olefins (Scheme 1, top and middle, respectively).[2,3] While both methods have been extensively studied and reviewed, the use of related sulfonyl halides and esters, giving similar transformations, gained only little attention (Scheme 1, bottom). Importantly, the three methods differ mechanistically: in the classical Julia approach radical fragmentation of *O*-acylated β-hydroxysulfones, followed by equilibration of transient vinyl radicals, leads exclusively to *E*-isomers of alkenes. Hetaryl sulfones add to carbonyl compounds followed by attack of the so formed alkoxide at the *ipso* position of the hetarene, which releases β-aryloxysulfinate via Smiles rearrangement. Then, the latter species *anti*-fragment to alkenes, phenol and sulfur dioxide. In turn sulfonyl halides and sulfonate precursors follow a path well-known for phosphorus-based olefinating reagents (e.g. in the Horner-Wadsworth-Emmons reaction), which consists of cyclization to 4-membered ring intermediates, which *syn*-fragment to the olefins. The mechanistic dichotomy is truly unprecedented among the olefination methods, and in our opinion deserves a specialized summary focused on the latter, least known, yet powerful method of synthesis of alkenes. Whereas early reports published in early 90s' were rather preliminary studies, this was changed in recent years with a series of publications, in which the 'overlooked' method was systematically explored.

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Scheme 1. Mechanistic summary of classical Julia olefination (top), one-pot Julia olefination (middle), and olefination with sulfonyl halides and esters discussed in this review (bottom).

2. Early Examples of Olefination with Sulfonyl Halides and Esters

The first example of applying carbanions derived from alkanesulfonates as olefination reagents was described by Hawkins.[5] In general, sulfonyl esters can be deprotonated at the α-position and the resulting carbanions add to the carbonyl group to obtain (after protonation) stable β-hydroxysulfonates. Inspired by a report of Martin on hypervalent sulfur compounds (Figure 1),[6-8] Hawkins hypothesized that the electronegative alkoxide in the sulfonate group could stabilize the penta-coordinated sulfur atom and therefore promote a new reaction pathway, involving cyclization of β-hydroxysulfonate *O*-anion, and fragmentation to alkene. Indeed, deprotonation of 2,2,2-trifluoroethyl methanesulfonate with BuLi (THF, -78˚C) followed by addition of benzophenone and warming of the reaction mixture to room temperature gave a 56% yield of the expected 1,1-diphenylethylene. The author proposed mechanism, which consists of attack of the sulfonate carbanion at the carbonyl group, then cyclization of β-hydroxysulfonate *O*-anion to 4-membered cyclic intermediate, and

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formation of the alkene via $[ROSO_3]^-$ elimination (Scheme 2, pathway *a*).[9] For a series of other fluoroalkyl or aryl mesylates, alkenes were also formed but with lower yields. It was noted that if OR is a good leaving group (like hexafluoroisopropoxide) a competitive elimination to sulfene predominates and alkene is not formed (Scheme 2, pathway *b*). The presented mechanistic scheme contained also alternative pathway of olefination including β-sultone, however the authors assumed that under described conditions such intermediate would undergo elimination to derivatives of vinylsulfonic acid rather than to alkene. Besides it was shown that intermediate β-hydroxysulfonate ester can be trapped at low temperature, but transforms into the alkene under basic treatment at higher temperatures.

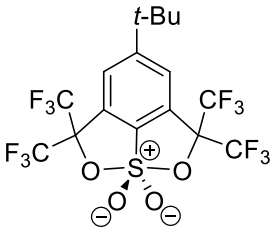
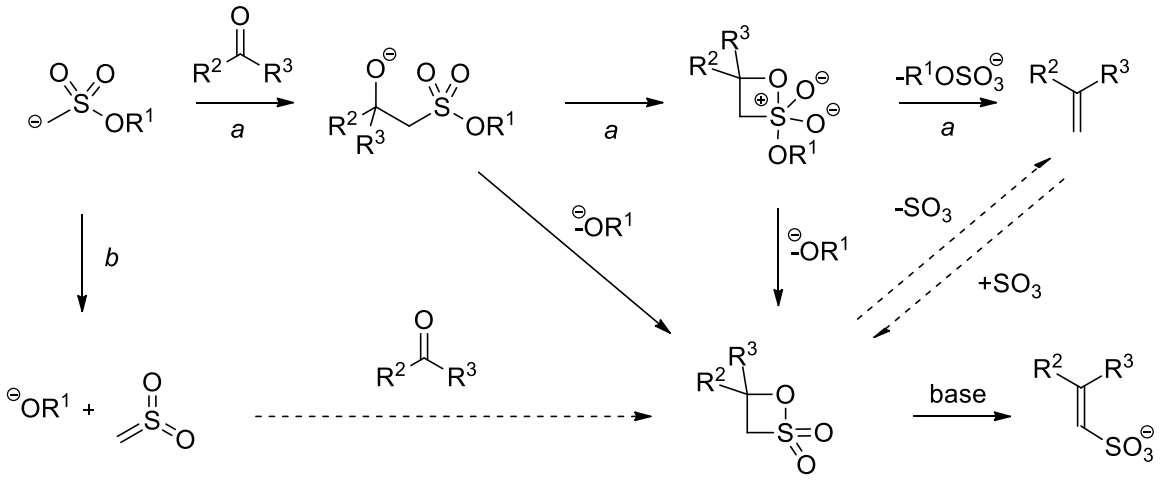


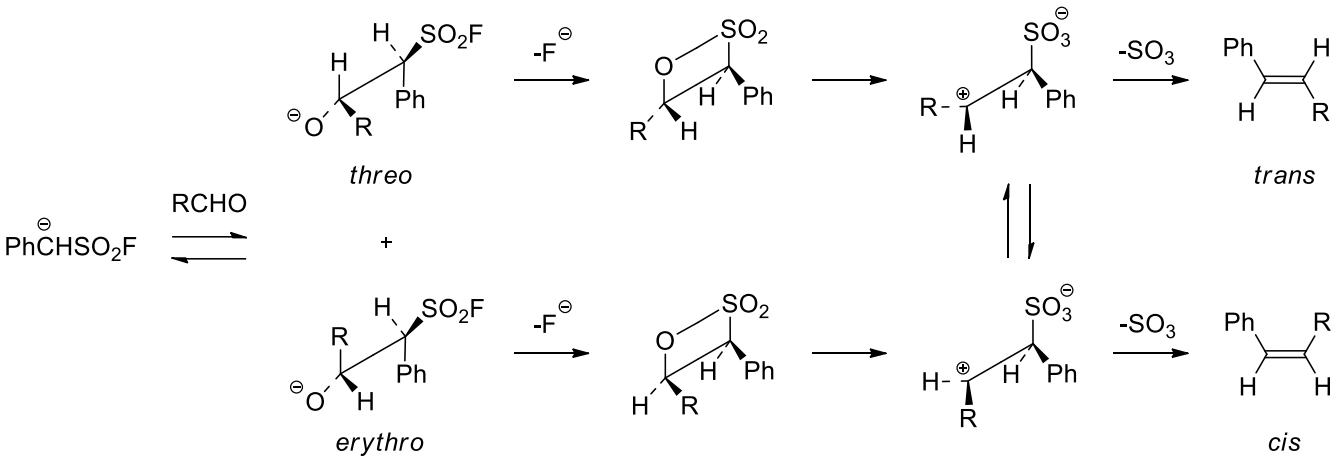
Figure 1. Example of compound containing penta-coordinated sulfur atom reported by Martin.[6]



Scheme 2. Mechanistic scheme of benzophenone olefination with alkyl and aryl mesylates proposed by Hawkins.[5]

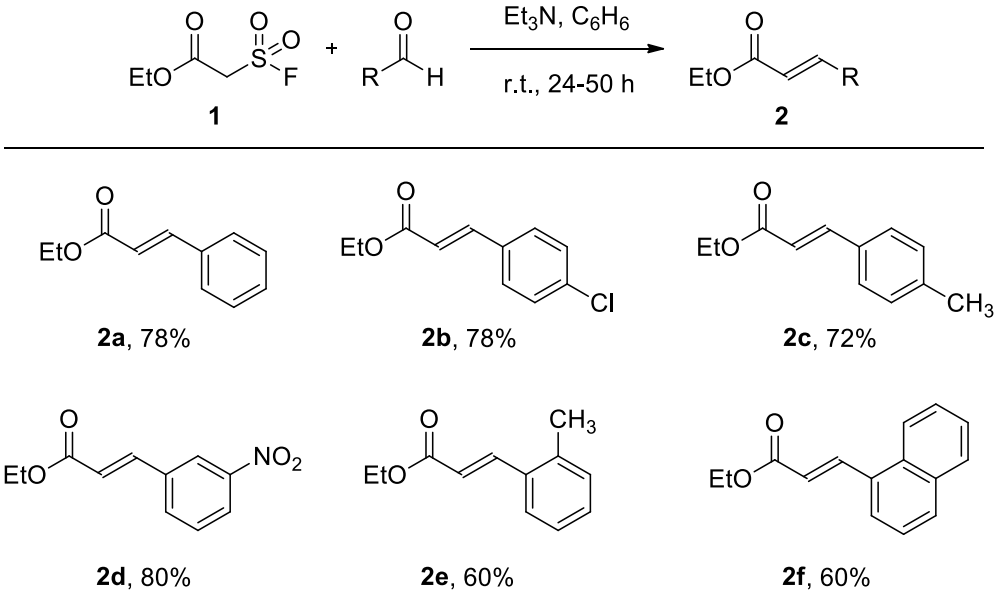
Shortly thereafter, a similar reaction of arylmethanesulfonyl fluorides with various aromatic aldehydes was described by Kagabu.[10] A series of substituted stilbenes was obtained under mild conditions (K_2CO_3 as a base with catalytic dibenzo-18-crown-6 in acetonitrile at room temperature) in moderate to good yields (44-84%). Higher yields were observed for aldehydes substituted with electron withdrawing groups. An effect of electrophilicity of the carbonyl group and type of the solvent on the *E/Z* ratio of alkenes was also noted. Unfortunately, under the described conditions non-stabilized methanesulfonyl fluoride condensed only slightly with benzaldehyde. Contrary to Hawkins,[5] Kagabu's proposed reaction mechanism involved formation of β-sultones, and their dissociation to zwitterionic species, which fragment to alkenes and SO_3 (Scheme 3).[10]

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Scheme 3. Mechanism of alkene formation via β-sultone intermediates proposed by Kagabu.[10]

Another paper by Kagabu *et al*. focused on the reactivity of arylmethanesulfonyl fluorides with α-bromoketones and activated bromoalkanes.[11] However, the authors demonstrated also that in reaction of more stabilized ethyl fluorosulfonylacetate (**1**) with various aldehydes a series of α,β-unsaturated esters **2a**-**f** was obtained under mild conditions (Scheme 4). Once again aldehydes with electron withdrawing substituents gave better yields. It was also exemplified that the stabilizing effect of the CO_2R group makes the carbanion derived from **1** much less nucleophilic (and therefore 'soft'), so that it preferentially substitutes the halide in phenacyl bromide, $PhC(=O)CH_2Br$, rather than attacking the carbonyl group.

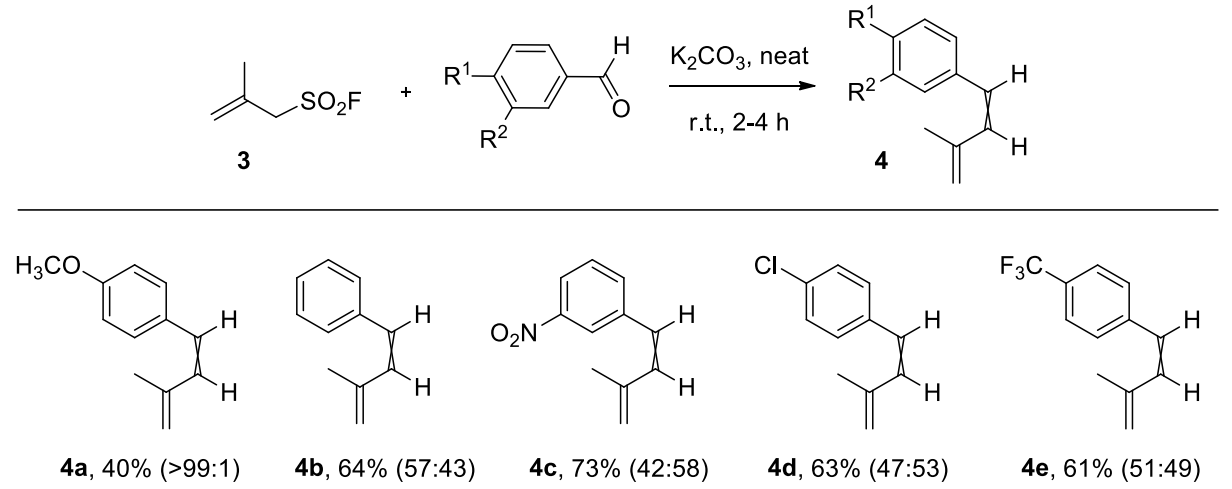


Scheme 4. Synthesis of α,β-unsaturated esters from fluorosulfonylacetate and aldehydes (products were reported as pure *E*-isomers).[11]

Years later, the Kagabu's protocol was used by Dubbaka and Vogel to obtain a series of dienes in the reaction of isobutenesulfonyl fluoride (**3**) with substituted benzaldehydes (K_2CO_3, 20 ˚C).[12] The desired products **4a**-**e** were obtained in moderate yields (40-73%), as mixtures of *E/Z* isomers, which were later *Z* → *E* isomerized in the presence of SO_2 (Scheme 5). For selected cases, olefination with structurally related

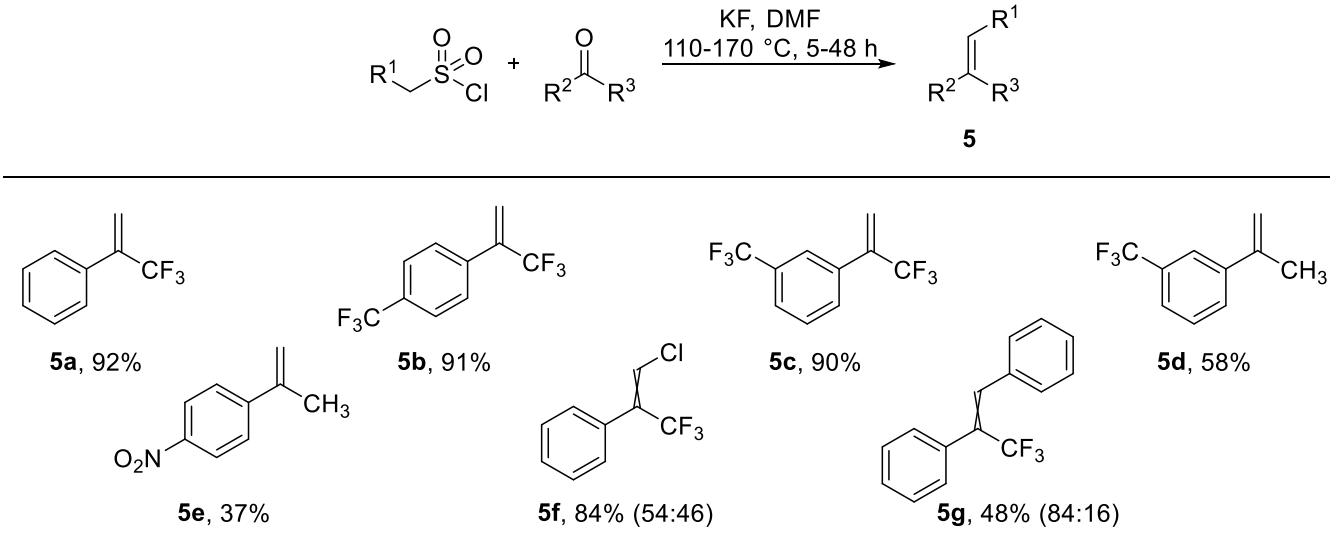
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sulfonates: 2,2,2-trifluoroethyl isobutenesulfonate (derived from trifluoroethanol) and 2,2,2-trifluoroethyl isobutenethiosulfonate (derived from CF_3CH_2SH) was also demonstrated.† In all examined cases a significant drop in the diene yields was observed (fluoride > ester > thioester).



Scheme 5. Synthesis of dienes using Kagabu's procedure and selected examples of obtained products (*E/Z* ratio was given in parentheses).[12]

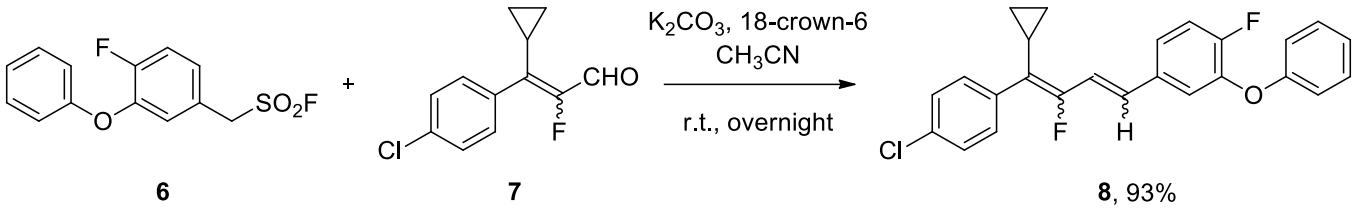
Another example of olefination using sulfonyl halides was described by Nader.[13] In this protocol alkanesulfonyl chlorides were reacted with substituted ketones in the presence of excess of KF (acting as a base and a source of fluoride) under relatively harsh conditions (DMF, 110-170 ˚C). In the initial step sulfonyl chloride might undergo displacement by F^- to give the corresponding sulfonyl fluoride, which could be the actual olefinating reagent. Yields of the obtained alkenes **5a**-**h** were highly dependent on the type of the carbonyl compound, with best results (> 90%) obtained for perfluoroalkyl-aryl ketones (Scheme 6). Similarly to Kagabu,[10] the reaction mechanism proposed by Nader involved formation of β-sultone, followed by elimination of SO_3, which yields alkene.[13]



Scheme 6. Synthesis of alkenes using Nader's procedure and selected examples of obtained products *(E/Z* ratio was given in parentheses).[13]

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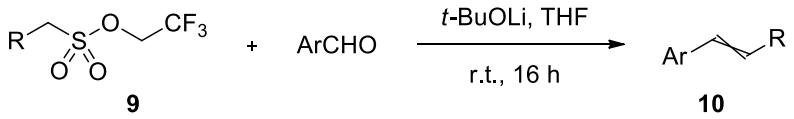
Selected references to the method were also presented in the patent claims. Reaction of arylmethanesulfonyl fluoride **6** with 3-aryl-2-fluoropropenal **7** (K_2CO_3, 18-crown-6, acetonitrile, r.t., overnight) was listed as a method for preparation of 1,4-diaryl-3-fluoro-1,3-butadienes **8** (Scheme 7).[14,15]

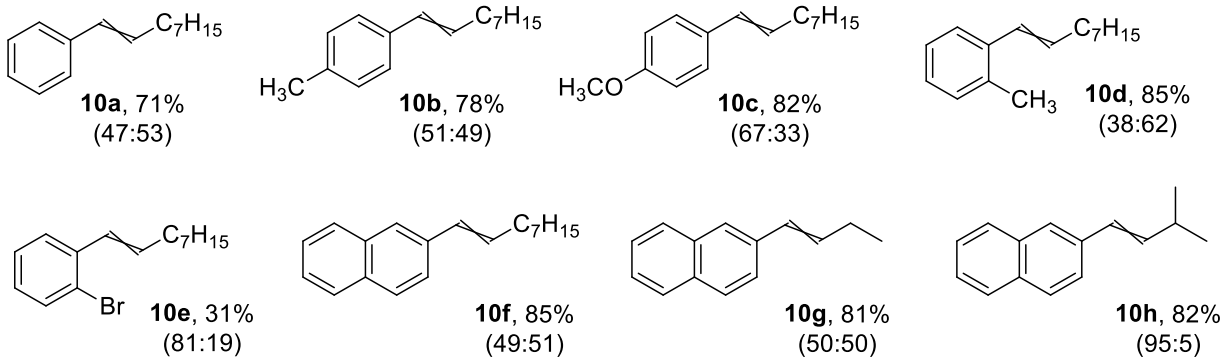


Scheme 7. Example of substituted butadiene synthesis from the patent claim (*E/Z* ratio was not reported).[14]

3. Systematic Exploration of Substrate Scope, Limitations and Reaction Conditions

Based on the available literature, our research group began a detailed systematic exploration of the olefination with sulfonyl halides and esters. Initially, the study focused mainly on reactions of non-stabilized carbanion precursors (alkanesulfonates) with non-enolizable aryl aldehydes.[16] 2,2,2-Trifluoroethyl alkanesulfonates **9** seemed to be the best reagents for this transformation compared to the corresponding sulfonyl chlorides and fluorides (carbanions of which appeared to be very unstable, and most likely eliminated to sulfenes), and neopentyl alkanesulfonates (which formed stable aldol-type adducts, but did not transform further to the olefins). The optimized procedure involved addition of *t*-BuOLi (2 equiv.) to the equimolar mixture of sulfonate and aldehyde dissolved in anhydrous THF under argon (so-called Barbier conditions), and stirring for 16 h at room temperature. In most cases, under these conditions alkenes **10a**-**h** were obtained in good yields, but with poor *E*/*Z* selectivities, mostly as equimolar mixtures of isomers (Scheme 8). Contrary to the results reported for sulfonyl halides,[10,13] reactions with EWG-substituted aryl aldehydes gave poor olefin yields.



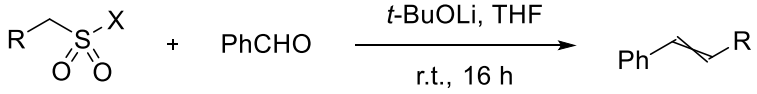


Scheme 8. Synthesis of alkenes using 2,2,2-trifluoroethyl alkanesulfonates and arylaldehydes under Barbier conditions (*E*/*Z* ratio of isolated products was given in parentheses).[16]

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Importantly, the practical potential of the method was demonstrated by preparation of **10a** from 2,2,2-trifluoroethyl octanesulfonate and benzaldehyde on a 100 mmol scale using concentrated lithium *tert*-amoxide (2-methyl-2-butoxide) and commercially available THF: alkene of excellent purity was isolated in 79% yield. It is also worth noting that the described protocol features a much easier removal of stoichiometric byproducts than popular olefination methods, like Wittig (Ph_3PO) or modified Julia olefination (ArOH).

In the next paper we focused on controlling of *E*/*Z* selectivity and application of more challenging, enolizable carbonyl compounds.[17] Attempts to control the stereoselectivity of the olefination began with a series of experiments subjecting a set of alkanesulfonates into the reactions with benzaldehyde under previously reported Barbier conditions (*t*-BuOLi, THF, 16 h, r.t.). Structures of the precursors varied with type of the leaving group (halides, esters), and stabilization of the carbanion center with alkyl (non-stabilized), phenyl (semi-stabilized) and ester (stabilized) functions (Scheme 9). Surprisingly, despite the application of a broad palette of (non-stabilized) octanesulfonates, the changes displayed practically no effect on the stereoselectivity, while obtained yields varied from 0 to 84% (for selected examples see Scheme 9, all data are available in Reference 17). On the other hand, differences between octanesulfonates and (semi-stabilized) phenylmethanesulfonates were huge, the latter giving predominant or exclusive *E*-isomer of stilbene in each case (although with various yields). In turn, stabilized derivatives of ethylsulfoacetate failed to give alkenes, likely due to the low nucleophilicity that disfavored the equilibrium of the aldol-type addition to benzaldehyde (supported by the fact that unreacted substrates were recovered in most cases).

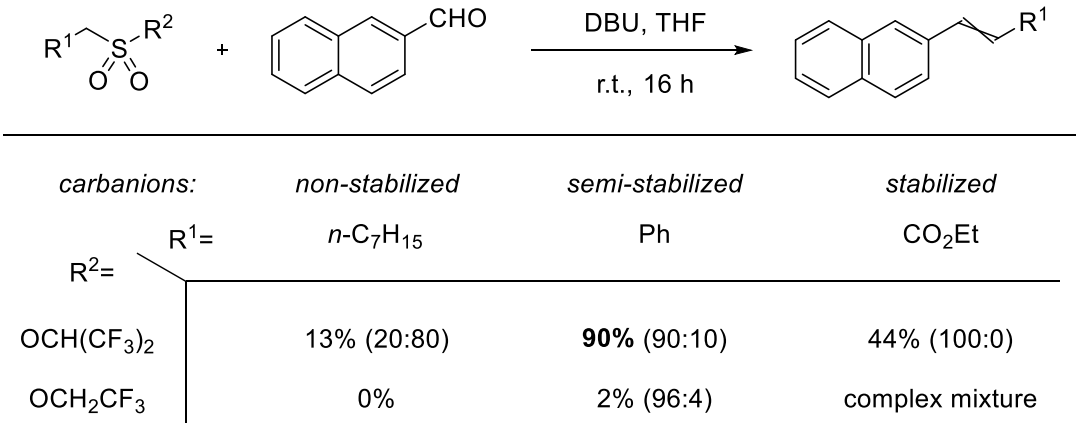


carbanions:	*non-stabilized*	*semi-stabilized*	*stabilized*
R= / X=	n-C_7H_{15}	Ph	CO_2Et
Cl	traces (73:27)	4% (79:21)	traces (100:0)
F	13% (40:60)	7% (89:11)	-
$OCH(CF_3)_2$	11% (47:53)	**76%** (100:0)	traces (100:0)
OCH_2CF_3	**84%** (46:54)	56% (100:0)	0%
OCH_2CCl_3	10% (56:44)	30% (99:1)	-
$OCH_2C(CH_3)_3$	0%	0%	0%

Scheme 9. Alkenes obtained using different types of carbanion precursors (*E*/*Z* ratio was given in parentheses, only selected cases were shown).[17]

For stabilized carbanion precursors the only success was achieved after switching the base to DBU. In the reaction of ethyl (1,1,1,3,3,3-hexafluoroisopropoxy)sulfonylacetate with model 2-naphthaldehyde (THF, r.t., 16 h), the α,β-unsaturated ester was obtained in a moderate 44% of yield.[18] However, under the same conditions, non-stabilized 1,1,1,3,3,3-hexafluoroisopropyl octanesulfonate gave only 13% of alkene, whereas 2,2,2-trifluoroethyl sulfonates gave practically no desired products (Scheme 10).

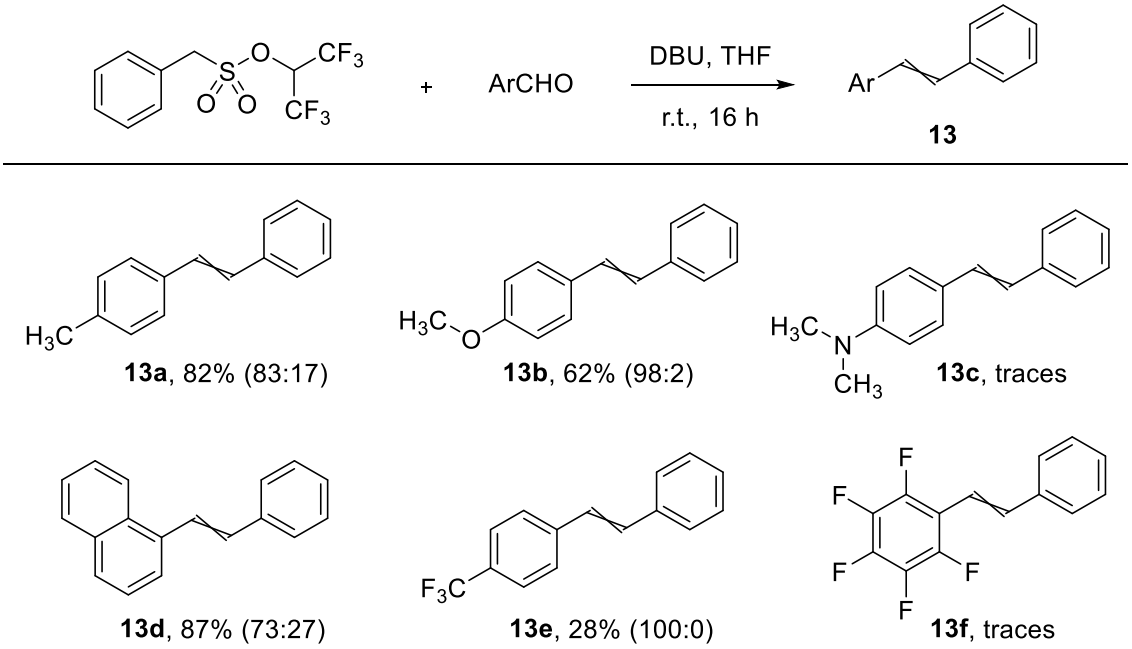
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carbanions:	*non-stabilized*	*semi-stabilized*	*stabilized*
R^1= / R^2=	n-C_7H_{15}	Ph	CO_2Et
$OCH(CF_3)_2$	13% (20:80)	**90%** (90:10)	44% (100:0)
OCH_2CF_3	0%	2% (96:4)	complex mixture

Scheme 10. Alkenes obtained using fluoroalkyl sulfonates and DBU as a base (*E*/*Z* ratio was given in parentheses).[17,18]

Since the procedure utilizing DBU was particularly successful for 1,1,1,3,3,3-hexafluoroisopropyl phenylmethanesulfonate this protocol was selected to examine influence of substituents in the arene ring of both substrates on the yields of stilbenes. Strongly electronically-altered benzaldehydes, such as pentafluorobenzaldehyde and *p*-(dimethylamino)benzaldehyde, gave only traces of desired products, whereas moderately tuned ones were well-tolerated (Scheme 11). On the other hand, substituents in the phenyl ring of the sulfonates displayed only little effect on the alkene yield, and a series of stilbenes was obtained with good yields (74-95%).

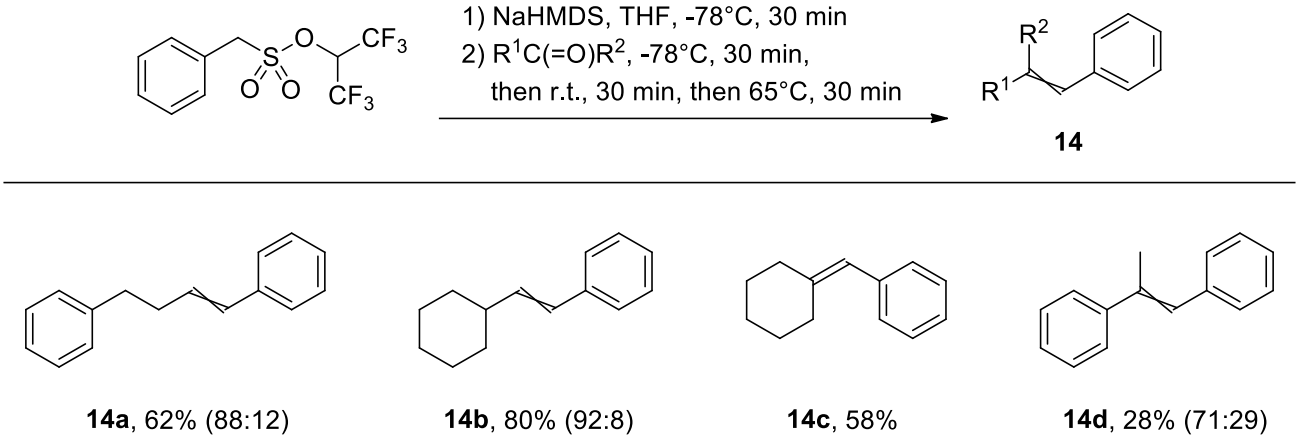


Scheme 11. Synthesis of stilbene derivatives using substituted aryl aldehydes (*E*/*Z* ratio was given in parentheses).[17]

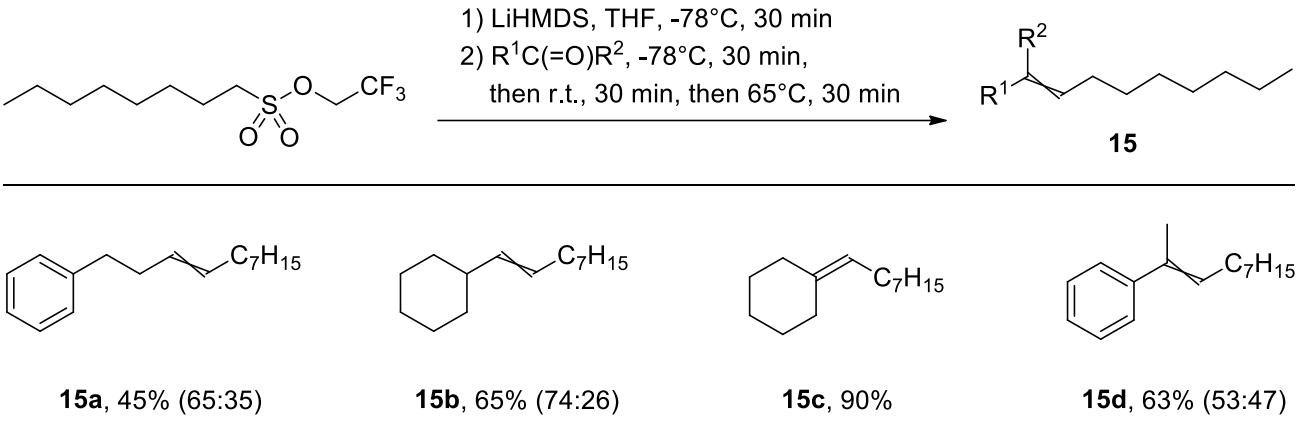
For olefination of more challenging enolizable aldehydes and ketones, the application of premetalated conditions was necessary. Carbanions were generated at -78 ˚C using hexamethyldisilazanes as bases

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(MHMDS, M = Na, Li), and after addition of carbonyl compound the mixture was stirred at r.t. for 30 min. However, we noticed that significant amounts of a polar fraction formed (likely containing intermediate aldol-type adducts), so in a modified procedure, stirring at r.t. for 30 min was followed by heating to 65 ˚C for 30 min. Indeed, in selected cases olefin yield was greatly improved. Under the optimized conditions two series of alkenes were obtained in the reactions of enolizable carbonyl compounds with semi-stabilized and non-stabilized precursors. In general, sodium base was more efficient for semi-stabilized precursors giving olefins with moderate to good yields and with enhanced *E*-selectivity (**14**, Scheme 12). In the case of non-stabilized trifluoroethyl alkanesulfonates, better results were obtained using LiHMDS, however stereoselectivity was in general lower (**15**, Scheme 13).



Scheme 12. Synthesis of alkenes by reacting semi-stabilized alkanesulfonate with enolizable carbonyl compounds and selected examples of obtained products (*E*/*Z* ratio was given in parentheses).[17]

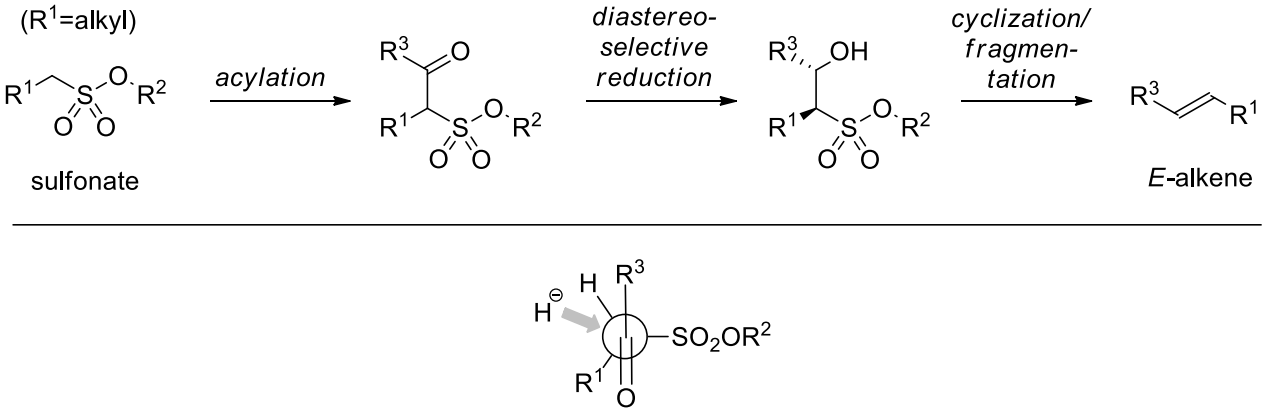


Scheme 13. Synthesis of alkenes by reacting non-stabilized alkanesulfonate with enolizable carbonyl compounds and selected examples of obtained products (*E*/*Z* ratio was given in parentheses).[17]

Another approach to improve the selectivity of alkenes produced in reactions of non-stabilized precursors was based on an alternative reaction pathway, which consists of acylation and diastereoselective reduction of the carbonyl group (Scheme 14, top).[19] We proposed that diastereomerically pure β-hydroxysulfonates may translate, after fragmentation, into pure isomers of alkenes. Interestingly, a similar approach was demonstrated by Jørgensen *et al.* for acylated benzothiazoyl sulfones, which were selectively reduced to

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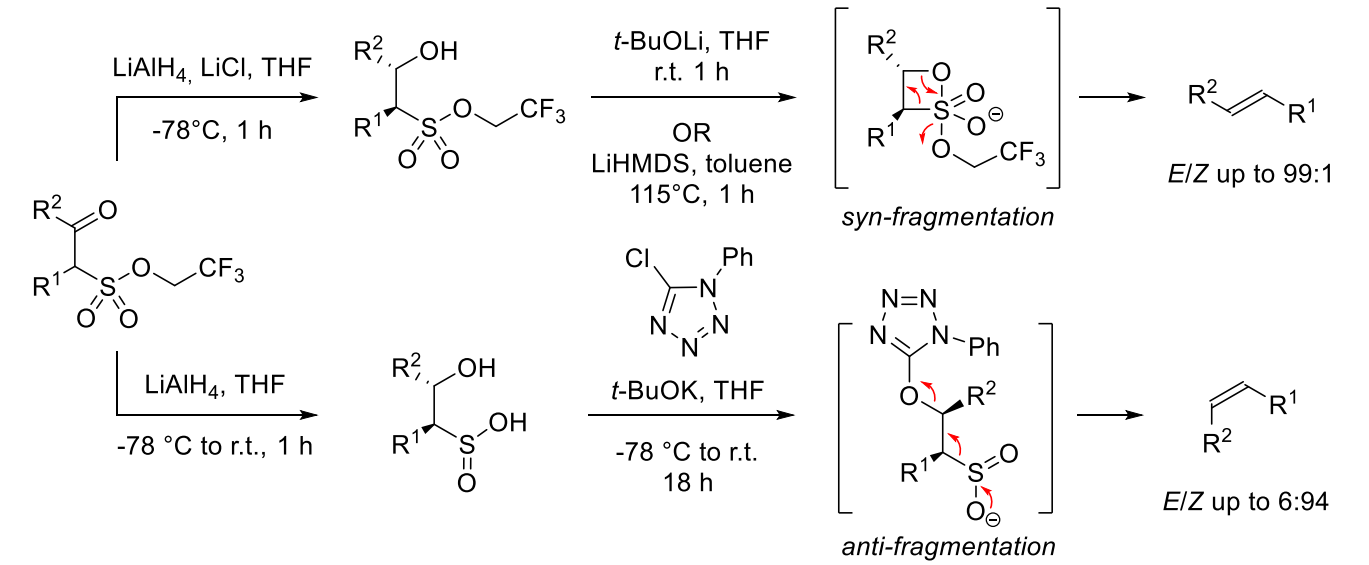
alcohols, and, following the 'one-pot' Julia olefination mechanism, transformed into isomeric alkenes.[20-22] In our case, acylated trifluoroethyl alkanesulfonates were reduced with $LiAlH_4/LiCl$‡ at -78 ˚C to obtain β-hydroxysulfonates with high diastereoselectivity. The reduction followed the Felkin-Ahn model, in which a large, electronegative sulfonyl group is located perpendicularly to the carbonyl moiety (Scheme 14, bottom). The so formed predominant isomers of β-hydroxysulfonates underwent fast cyclization/fragmentation to *E*-alkenes under basic conditions.

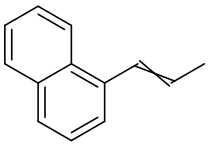
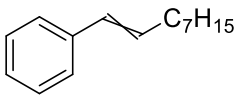
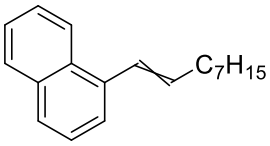
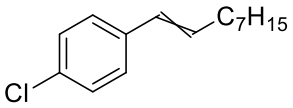
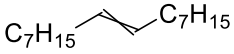
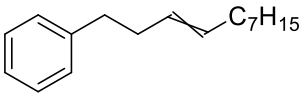


Scheme 14. Conceptual scheme for stereoselective alkene synthesis (top), and Felkin-Ahn model for the carbonyl group reduction (bottom).[19]

During optimization of the reduction conditions, we observed that warming up the reaction mixture to r.t. produces another product − β-hydroxysulfinic acid, product of subsequent reduction of the sulfonyl group. We assumed that this process retains high diastereoselectivity of the initial carbonyl reduction, and therefore may pave the way for alternate fragmentation mechanism, leading to the olefin of the opposite configuration (inspired by the 'one-pot' Julia olefination). Indeed, basic treatment of the β-hydroxysulfinic acid in the presence of 5-chloro-1-phenyl-1*H*-tetrazole led to activation of hydroxyl group toward *anti*-fragmentation, and gave alkene with high *Z*-selectivity. Combination of these two pathways constituted a stereodivergent protocol, allowing selective synthesis of *E*- or *Z*-alkenes in a 3-step transformation of alkanesulfonates with single chromatographic purification of the final product (Scheme 15). Using a broad palette of substrates, over a dozen alkenes was obtained with good (for *E*-selective pathway) and moderate (for *Z*-selective pathway) yields. Additionally, during screening of reducing agents, another transformation of acylated sulfonates was discovered: reaction with tetrabutylammonium borohydride in DMF at 85 ˚C led to selective cleavage of the whole $SO_2OCH_2CF_3$ group with the formation of ketones.

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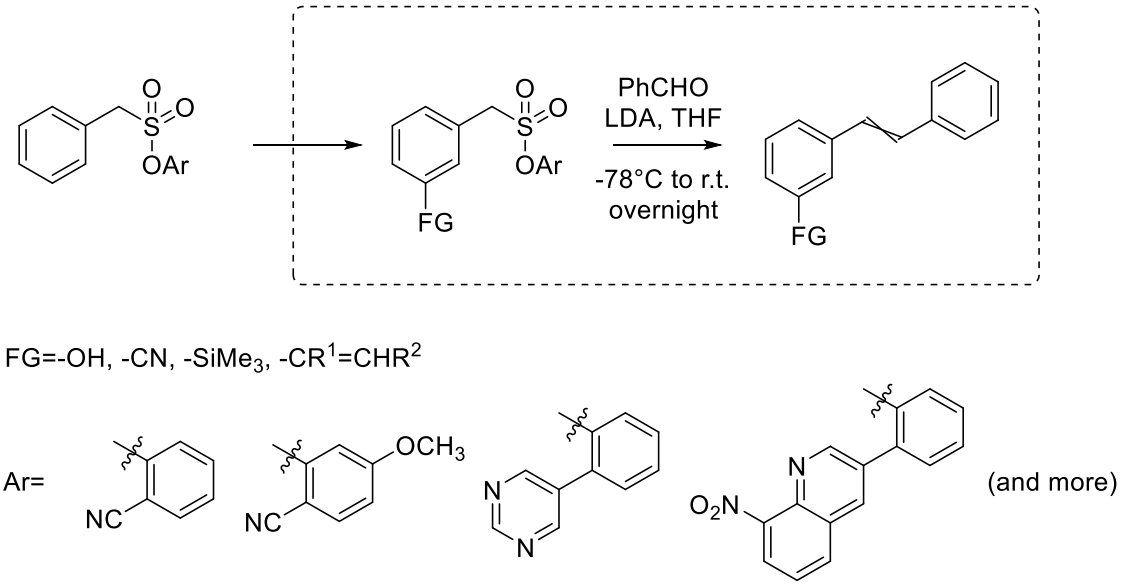


	E-selective protocol	*Z*-selective protocol		*E*-selective protocol	*Z*-selective protocol
	82% (97:3)	53% (8:92)		85% (98:2)	55% (6:94)
	81% (95:5)	50% (16:84)		87% (98:2)	53% (8:92)
	69% (90:10)	53% (7:93)		66% (89:11)	41% (10:90)

Scheme 15. Stereodivergent protocol for *E*- and *Z*-alkenes using acylated alkanesulfonates (olefin yields over three steps, *E*/*Z* ratio was given in parentheses).[19]

A careful search in databases of recent literature revealed also transformations of arylmethanesulfonyl esters with aldehydes, reported by Maiti *et*. *al*. (Scheme 16). The pathway was applied for removal of the sulfonyl moiety, however the process was imprecisely described as 'modified Julia olefination'. Sulfonyl esters of substituted phenols were used as directing groups for transition metal-catalyzed *meta*-functionalization of arenes: hydroxylation,[23] alkenylation,[24-26] silylation[27] and cyanation.[28] Then the sulfonyl ester moiety might be removed by reacting functionalized arylmethanesulfonates with aryl aldehydes under mild conditions, which lead to the formation of substituted stilbenes. A similar approach was described by Yu, who used sulfonamide as a *meta*-directing group for palladium-catalyzed arene alkylation and arylation.[29] After successful functionalization, the sulfonamide moiety was also removed via carbonyl olefination.

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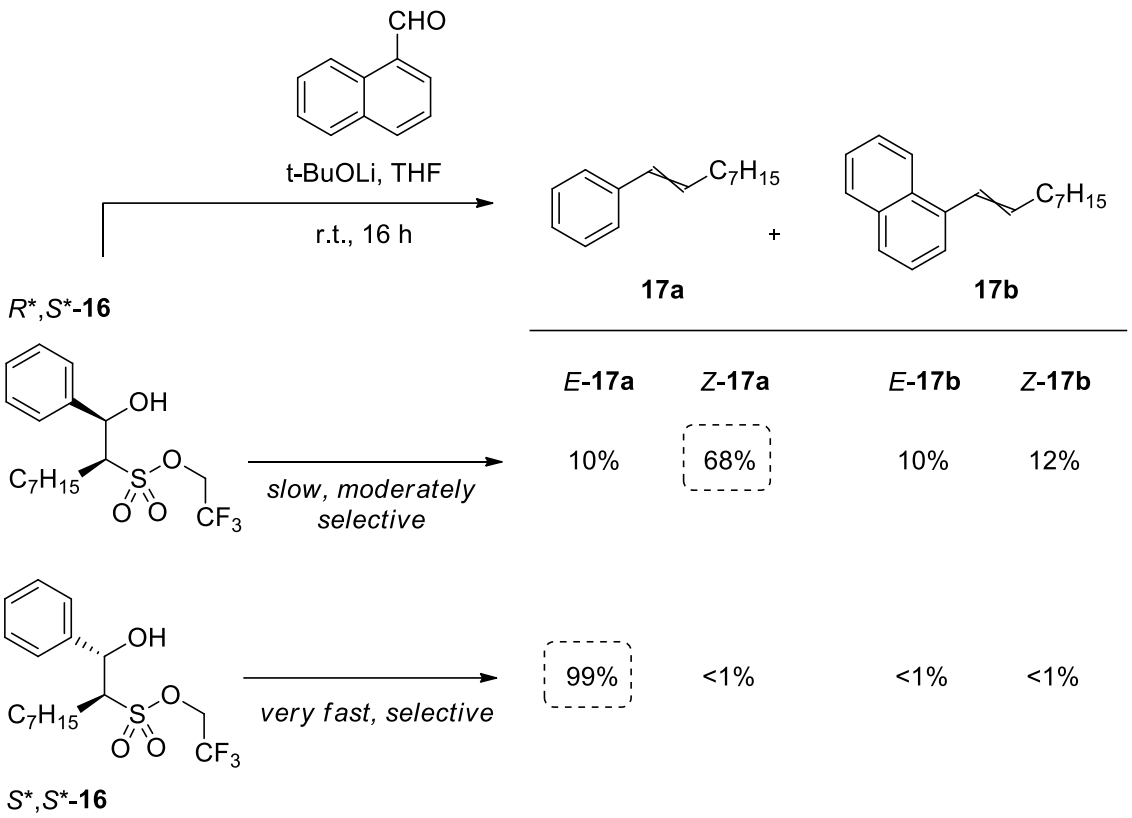


Scheme 16. General synthetic scheme described by Maiti.[23-28]

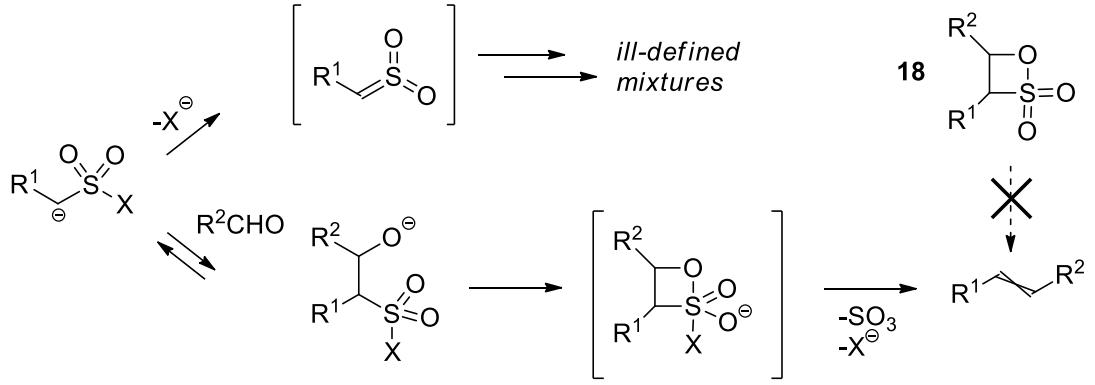
4. Mechanistic Findings

For a better understanding of the mechanism of the olefination with sulfonyl halides and esters, and factors controlling its selectivity, we performed numerous mechanistic experiments.[16,17] Intermediate aldol-type adducts **16** of non-stabilized 2,2,2-trifluoroethyl 1-octanesulfonate with benzaldehyde were isolated as single diastereoisomers, and subjected to the reaction conditions with another aldehyde. On the basis of the postulated mechanism, the adducts should cyclize and *syn*-fragment to individual isomers of alkenes. Surprisingly, it turned out that the diastereoisomers significantly differed in reactivity. A major isomer *R**,*S**-**16** reacted slowly, giving a mixture of alkenes containing mainly *Z*-**17a**, but also a substantial amount of *E*-**17a** and cross-products *E*- and *Z*-**17b**. This indicated that the system has enough time for equilibration of the aldol reaction, and therefore the overall selectivity is diminished. On the other hand, minor diastereoisomer *S**,*S**-**16** reacted very fast and almost exclusively gave *E*-**17a** (Scheme 17). Accordingly, a corrected version of the mechanism was proposed, where a combination of stereoselective fragmentation of minor aldol-type adduct to *E*-alkene, and moderately selective fragmentation of major isomer accompanied with aldol-type equilibration resulted in the observed formation of equimolar mixtures of alkene isomers. In another mechanistic experiment β-sultone **18**, a four-membered cyclic sulfonate prepared independently from alkene and SO_3, failed to give alkenes under the reaction conditions that suggested fragmentation of the initially-formed structure containing a penta-coordinated sulfur atom, prior to release of the trifluoroethoxide (Scheme 18). The process of olefination was also the subject of preliminary *ab initio* calculations,[30] which confirmed that the formation of four-membered cyclic intermediate containing penta-coordinated sulfur atom has a low energy barrier, in support of the presented mechanism.

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Scheme 17. Reactivity of aldol-type adducts with non-stabilized carbanion precursor.[16]

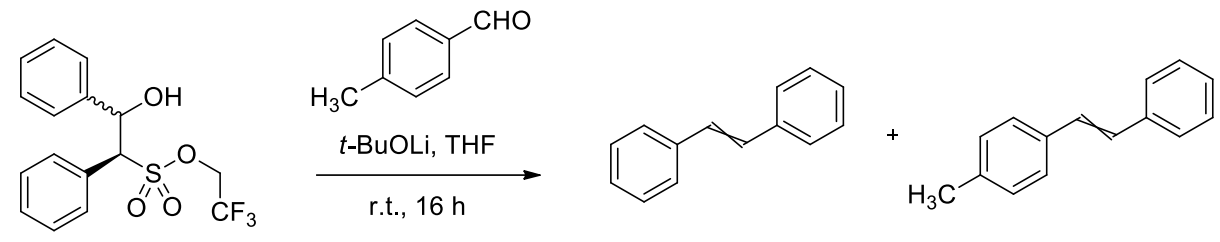


Scheme 18. Mechanistic scheme of olefination with sulfonyl halides and esters proposed by our group.[16]

The hypothesis of less favored aldol equilibrium for carbanions derived from semi-stabilized precursors was supported by similar studies of reactivity of the aldol-type adducts with trifluoroethyl phenylmethanesulfonates.[¥] The intermediates, isolated as pure diastereoisomers and subjected to the olefination conditions, reacted similar to each other (in contrast to non-stabilized analogues shown at Scheme 17), and produced significant amount of cross product, formed as predominant *E*-isomer (Scheme 19). The result was consistent with the scenario of much faster equilibration (related to a less favored equilibrium of the aldol-type addition), and kinetically preferred transformation of one isomer, fragmenting to the *E*-alkene. So, the difference between non-stabilized and semi-stabilized precursors in terms of selectivity of the alkene formation arises from different rates of equilibration between unselectively formed diastereoisomers of the adducts, and inherited preference of one of them for faster fragmentation to alkene (*E*-isomer). The easier the

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equilibrium is established, the higher selectivity is observed, and under the Curtin-Hammett regime it originates exclusively from the relative rates of cyclization-fragmentation of adducts, rather than the isomer ratio of formation of the intermediate aldol-type adducts.



18 **19a** **19b**

	E-**19a**	*Z*-**19a**	*E*-**19b**	*Z*-**19b**
*R**,*S**-**18** ⟶	44%	<1%	55%	<1%
*S**,*S**-**18** ⟶	51%	<1%	48%	<1%

Scheme 19. Reactivity of aldol-type adducts of semi-stabilized carbanion precursor.[17]

Finally, less general mechanistic findings concerning the chemistry were presented in original reports, and accompanying supporting information files.[16,17,19]

5. Conclusions

Although the first reports about olefination of carbonyl compounds with sulfonyl halides and esters were published in the early 90s', the methodology was only recently systematically studied. In a series of articles, a number of factors affecting stereoselectivity and alkene yield were studied. The reaction mechanism involving formation of a four-membered intermediate containing a penta-coordinated sulfur atom was confirmed, and procedures for olefination using different types of carbanion precursors and carbonyl compounds have been optimized. Finally, by applying alternative acylation/reduction pathway, the described methodology was demonstrated as a stereodivergent protocol, allowing preparation of alkenes with high *E*- and *Z*-selectivity, depending on the reaction conditions. The chemistry expands the armory of synthetic methods for the synthesis of alkenes, supplements the methodology of Julia olefination reactions, and broadens knowledge of the reaction mechanisms.

Acknowledgements

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Notes and References

† It must be noted that olefination with sulfonyl ester and thioester was performed using different protocol (*t*-BuLi, -78 → 20 ˚C), as compared with reactions of sulfonyl fluoride (K_2CO_3, 20 ˚C).
‡ Addition of LiCl was necessary to inhibit deprotonation of the acylated sulfonate, which resulted in its partial recovery (see ref. 19 for details).
¥ It should be noted that arylmethanesulfonates display not only electronic stabilization of carbanions, but also increased steric effects, as compared with (linear) alkanesulfonates. Thus, both factors are responsible for the observed faster equilibration of their aldol-type adducts.

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