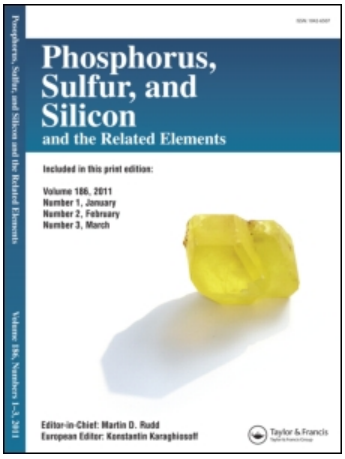

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Recent Sulphone-Based Olefination Reactions

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RECENT SULPHONE-BASED OLEFINATION REACTIONS

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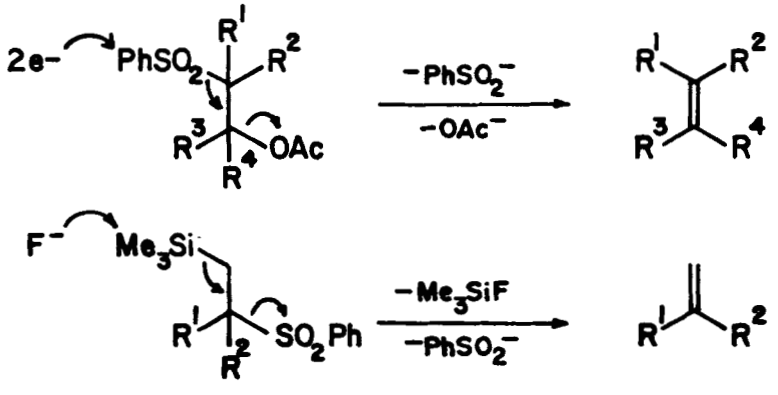
Abstract The scope, limitations, and recent applications of two olefination reactions based on the reductive elimination of β-acyloxy sulphones (the Julia olefination) and the fluoride-induced elimination of β-trimethylsilyl sulphones is reviewed.

INTRODUCTION

The union of two fragments with concomitant regiospecific formation of a double bond is a common synthetic goal. The Wittig reaction and related phosphorus-based methods provide typical solutions to such problems as they are connective, regiospecific, and capable (up to a point) of stereochemical manipulation. Unfortunately, for various reasons these abundant virtues could not be used to advantage in several of our synthetic programmes and so alternatives were required. This review summarises some of our experiences with two such alternative ole-



Scheme 1

finations based on eliminations of arylsulphinate anion from β-substituted sulphones. These methods are summarised in Scheme 1.

THE JULIA OLEFINATION

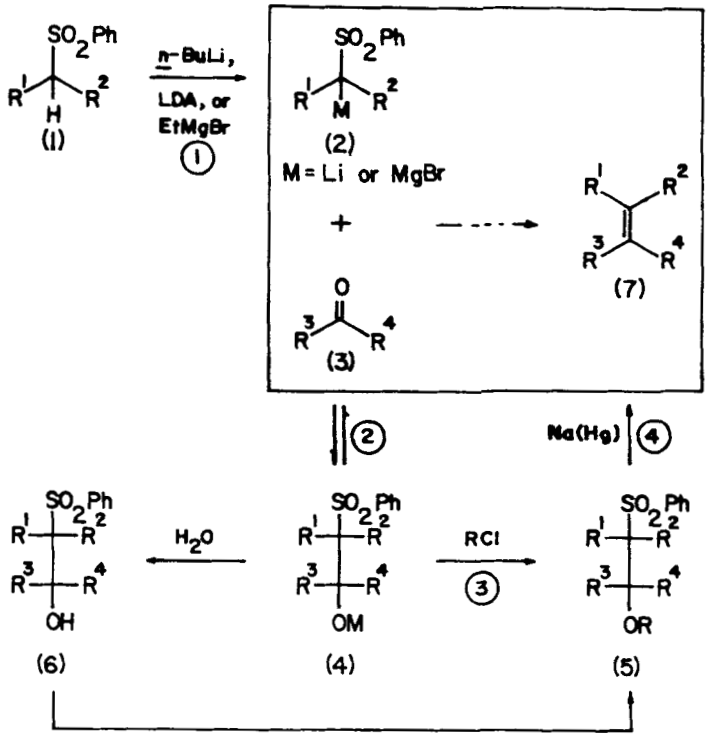
In 1973 Julia and Paris [1] reported a new sulphone-based olefination sequence which, like the Wittig reaction, was connective and regiospecific. The Julia olefination consists of four distinct stages as summarised in Scheme 2:

1. α-Metalation of a phenyl alkyl sulphone (1).
2. Condensation of the α-metallated sulphone (2) with an aldehyde or ketone to give a β-phenylsulphonyl alkoxide adduct (4).
3. Functionalisation of the adduct (4) to give (5).
4. Reductive elimination of the β-substituted sulphone (5) with sodium amalgam.

The first three stages can be performed in a single reaction vessel although the overall efficiency of the sequence can be improved by isolating the β-hydroxy sulphone (6) and functionalising the hydroxyl group in a separate step. Purification of intermediates is not normally required. Table 1 gives an indication of the olefins accessible by this route.

By comparison with the Wittig reaction the Julia olefination has two principal assets. First, as the nucleophilic partner in the connective step (stage 2) sulphones are used which are often more readily available than the corresponding phosphonium salts. Secondly, the 1,2-disubstituted olefins produced in the reductive elimination step have predominantly the trans-geometry. One detraction of the Julia olefination is its length - it

can be foiled at any one of the four stages delineated in Scheme 2. In practice stage 2 is usually the most problematic and stage 4 the least. However, in certain circumstances all of the stages have their pitfalls and



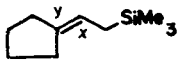
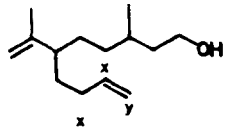
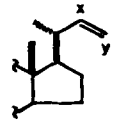
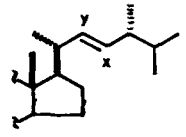
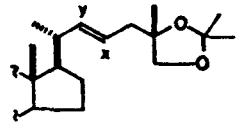
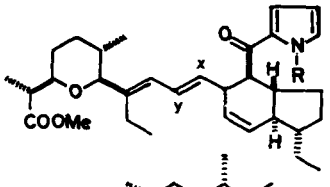
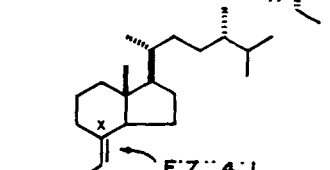
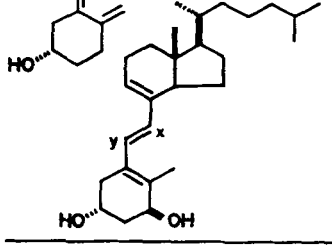
Scheme 2

these will be discussed individually.

Stage 1 α-Metalation of the Sulphone

Aryl alkyl sulphones are about as acidic as esters. They react rapidly with n-BuLi or lithium di-isopropylamide (LDA) in tetrahydrofuran (THF) at -78°C to give homogeneous solutions of α-lithiated sulphones (2) (M = Li) which are bright yellow in the case of simple aryl alkyl sulphones to red-orange in the case of aryl allyl sulphones. The corresponding magnesium derivatives (2) (M =

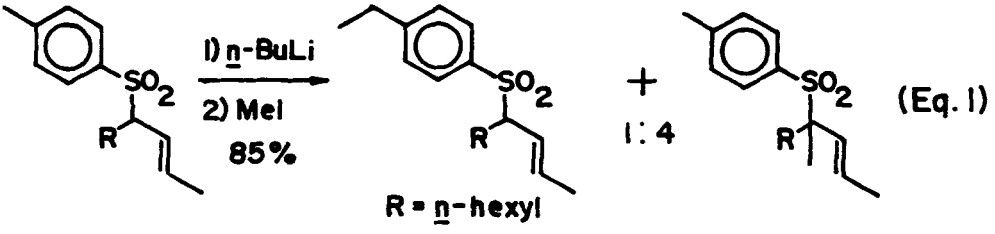
TABLE 1 Representative olefins prepared by the Julia reaction.

Olefin[a]	y	Yield (%)	Ref
	OSO_2Me	94	2
	AcO	56	3
	OH	77	4
	AcO	31	5
	OSO_2Me OH	77 69	6
	OBz	53	7
	OBz	56	8
	OBz	80	9

[a] x and y represent the site of the arylsulphonyl and leaving groups respectively in the β-substituted sulphones.

MgBr) are prepared by addition of EtMgBr to a solution of the sulphone in benzene or THF followed by a brief period under reflux. The resultant faintly coloured magnesio derivatives are often insoluble in the reaction medium and separate from solution as gums which can be difficult to stir.

Problems have been encountered when phenyl alkyl sulphones with highly hindered α-protons were treated with n-BuLi. A competitive abstraction of the proton ortho to the sulphone function on the benzene ring took place in which case LDA was the preferred base. Similarly, hindered p-tolyl alkyl sulphones can undergo deprotonation of the aromatic methyl group as demonstrated in Eq. 1. This is unfortunate because p-tolyl sulphones are more often crystalline then the corresponding phenyl derivatives.



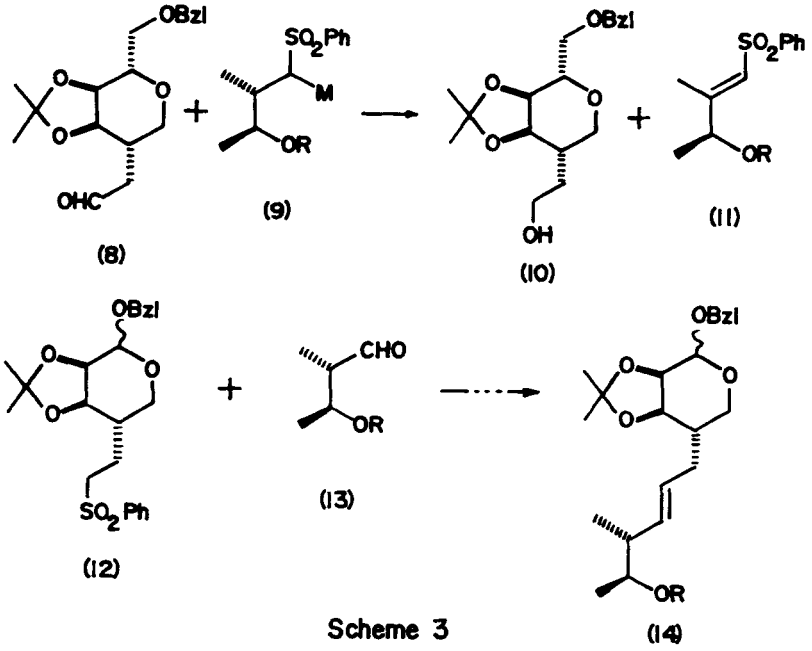
Stage 2 Condensation of the α-metallated sulphone with Aldehydes and Ketones

The principal cause of failure in the Julia olefination results from an unfavourable equilibrium at stage 2 which is most pronounced when the adduct (4) is steri-

cally encumbered. Adducts derived from ketones are more vulnerable than those derived from aldehydes [10]. One factor governing adduct stability is the metal counter-ion. Thus adduct (4) (M = Li, R^1 = n-heptyl, R^3 = n-hexyl, R^2 = R^4 = H) is unstable and cannot be trapped whereas the same adduct (M = MgBr) can be isolated as a 3 : 2 mixture of diastereomeric β-acetoxy sulphones after treatment with acetic anhydride [11].

However, other factors must also contribute significantly to condensation of the anion and carbonyl fragments as shown by the fact that anion (9) (Scheme 3, M = Li) condenses with isobutanal to form an adduct which can be trapped as a diastereomeric mixture of acetates whereas a similar sequence of reactions using propanal failed to give an adduct under similar conditions.

An interesting divergence in behaviour of lithium and magnesium derivatives of the sulphone (9) has emerged from recent studies on the synthesis of the pseudomonic acid family of antibiotics. The lithio derivative (9) failed in our hands [12] to condense efficiently with aldehyde (8); the magnesio derivative (9) on the other hand behaved as a reducing agent giving (10) and (11) (Scheme 3). However by reversing the functionality, fragments (12) and (13) were successfully condensed to give the desired trans-olefin stereoselectively in (14) [13]. It is noteworthy that attempts to introduce the trans olefin in analogous systems using the Wittig reaction gave poor stereoselectivity and yield [14].



Scheme 3

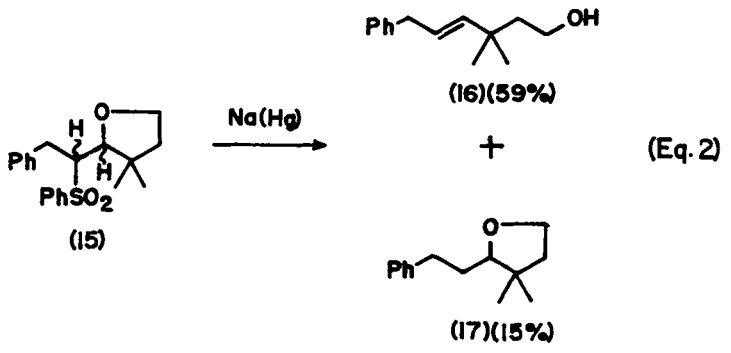
Stage 3 Functionalisation of the adduct

Reductive eliminations of β-hydroxy sulphones to olefins are known [1,4,6,15-18] but they usually occur rather slowly even at room temperature. In order to minimise side reactions such as retroaldolisation of the β-hydroxysulphone or reductive desulphonylation, the hydroxyl group can be converted to an acetate, benzoate, or methanesulphonate. For simple olefins the methanesulphonate is preferable as it is less sensitive to reaction with the basic solvent in the next step (vide infra) and yields in the subsequent step are usually slightly better. However, adducts derived from α,β-unsaturated aldehydes are better protected as the acetate or benzoate since allylic methanesulphonates are not robust.

Stage 4 Reductive elimination

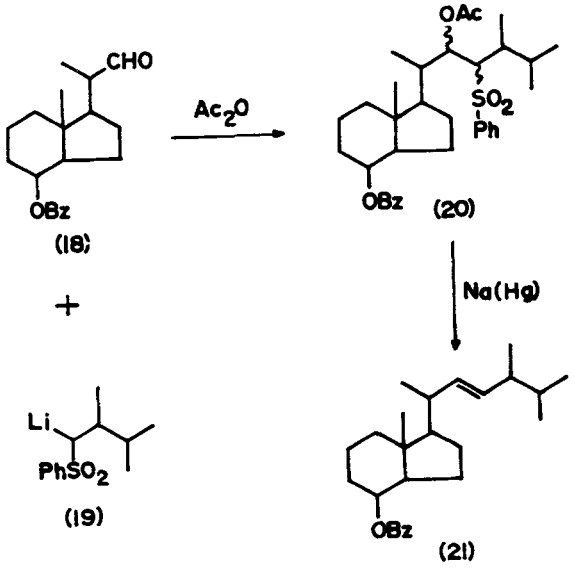
The reductive elimination step is effected by adding an excess of 5.65% sodium amalgam (2.5 mg atom of Na/g) to an efficiently stirred solution of the sulphone in 3 : 1 THF-MeOH at $-20^{\circ}C$. The reaction is easily monitored by thin layer chromatography until complete (usually 1-5 h). Additional sodium amalgam may be needed for longer reactions. Our choice of solvent and temperature was the result of a detailed study [11] in which it was found that a protic solvent was essential and that MeOH was superior to EtOH or i-PrOH at $-20^{\circ}C$. The THF was added to improve solubility of organic substrates at the low temperature and diminish the rate at which the sodium amalgam reacted with the MeOH. The formation of NaOMe - an agent of serious side reactions - is slow at $-20^{\circ}C$ and its effects can be suppressed by the addition of NaH_2PO_4 as a heterogeneous base scavenger [4,19].

The rate of reductive elimination can vary considerably depending on the β-substituted sulphone. Formation of conjugated dienes and trienes is fast - especially when the sulphone occupies an allylic position. Although methanesulphonates, benzoates, and acetates react at roughly similar rates, reductive elimination of β-alkoxy sulphones requires higher temperatures and longer reaction times. For example the cyclic ether (15) (Eq.2) required a large excess of sodium amalgam for 48 h to effect conversion to (16) and (17) [20].



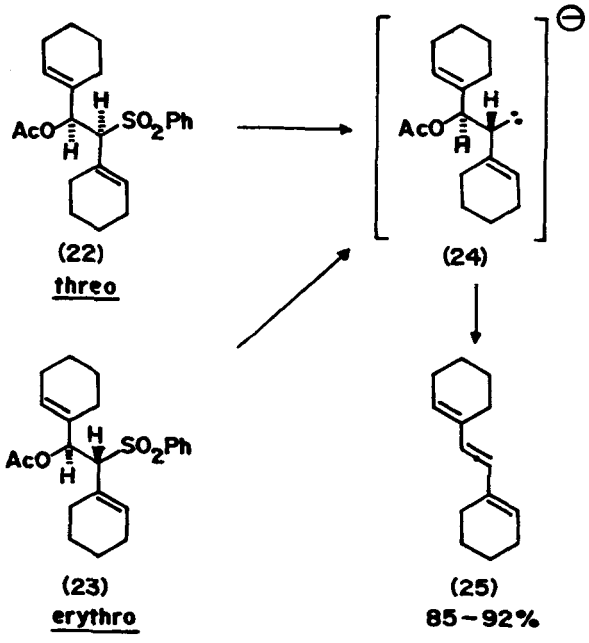
Stereochemistry

A synthesis of (21), a key fragment of Vitamin D_2[21] (Scheme 4) first revealed that the Julia reaction affords predominantly trans-1,2-disubstituted olefins. Thus, acetylation of the intermediate derived from union of fragments (18) and (19) gave a 1:1 mixture of diastereomeric β-acetoxysulphones (20) which, without separation, was treated with sodium amalgam in the usual way to give the desired fragment (21) as a single trans isomer in 45% overall yield. That the stereochemistry of the product was independent of the stereochemistry of the



Scheme 4

β-acyloxy sulphone was subsequently verified by treating the individual threo and erythro diastereoisomers (22 and 23 respectively)(Scheme 5) with sodium amalgam under identical conditions to give exclusively the trans-triene (25) [11].

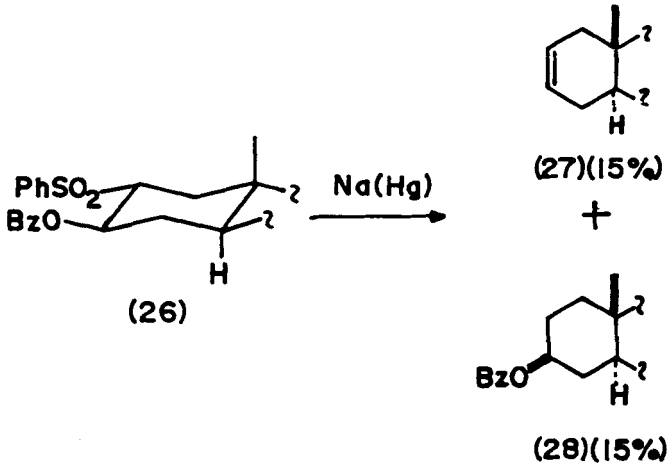


Scheme 5

The stereochemical results can be interpreted (Scheme 5) in terms of an intermediate carbanion (or radical) (24) derived from electron transfer from the metal to the sulphone group followed by elimination of benzenesulphinate anion (or benzenesulphinyl radical) in which the p-orbital is trans-coplanar to the acetoxy group and the bulky substituents as far apart as possible. According to this view the overall stereochemistry is governed by steric interactions of the substituents and assumes that the species (24) has sufficient lifetime to

equilibrate. There are two further implications: firstly, the olefins obtained should represent the thermodynamic mixture and secondly, increased branching, especially on those carbons adjacent to the carbons bearing the arylsulhpnyl and the acyloxy groups should increase stereoselectivity [22]. As can be seen from Table 2 this is the case. Furthermore, it can be seen also from entries 2 and 3 that interchanging the position of the sulphone and the acyloxy groups has no effect on the stereochemical outcome of the reaction.

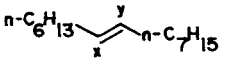
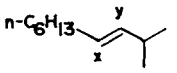
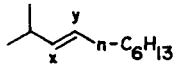
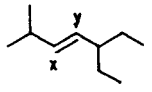
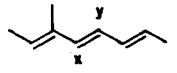
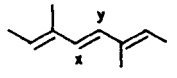
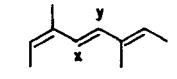
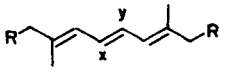
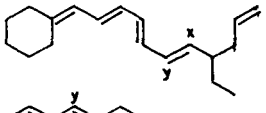
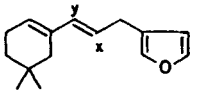
Adverse conformational effects can affect the reductive elimination. For example, in the cholestane derivative of (26) (Eq.3) the trans-diequatorial substituents can-



(Eq.3)

not achieve a trans-coplanar relation demanded by the mechanism in Scheme 5 unless the ring undergoes an unfavourable conformational change to a boat. Consequently only a 15% yield of cholest-2-ene (27) was obtained along with 15% of benzoate (28) derived from protonation of the carbanion before elimination could occur. It is noteworthy that the reductive elimination of (26) was unusually slow at -20°C and could only be effected with a lar-

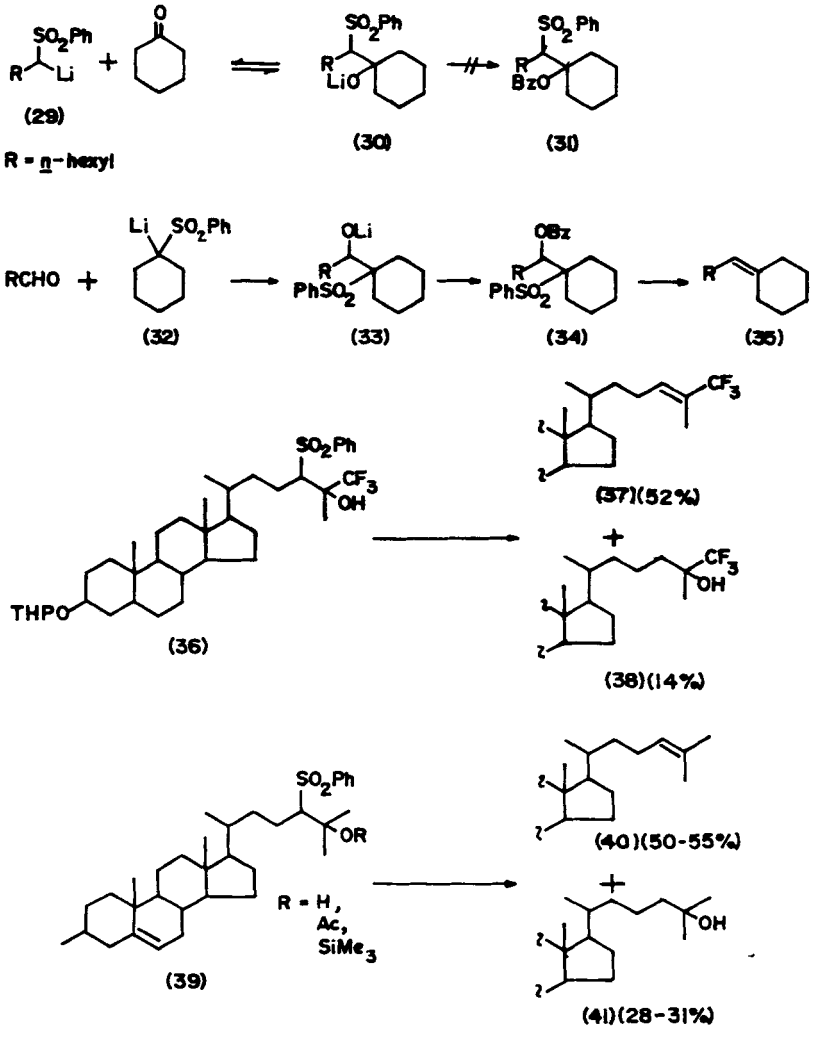
TABLE 2 The influence of chain branching on the stereochemistry of the Julia reaction.

Entry	Olefin[a]	Trans:cis	Yield (%)
1		8:2	53[b]
2		9:1	63[b]
3		9:1	68[b]
4		100:0	71[b]
5		97:3	68[b]
6		98:2	61[b]
7		98:2	75[b]
8		8:2	90[b]
9		10:1	49[c]
10		6:1	65[d]

[a] x and y represent the site of the arylsulphonyl and acyloxy groups respectively in the β-acyloxysulphone.
[b] Reference 22.
[c] W.R.Roush and S.M.Peseckis, Tetrahedron Lett., 1982, 23, 4879.
[d] Y.Masaki, K.Hashimoto, Y.Serizawa, and K.Kagi, Chemistry Lett., 1982, 1879.

ge excess of sodium amalgam at room temperature. This suggests that there may be a stereoelectronic advantage in the reductive elimination in a coplanar relation between the arylsulphonyl and the acyloxy groups.

A serious obstacle to the use of the Julia olefination for the synthesis of tri-substituted double bonds is

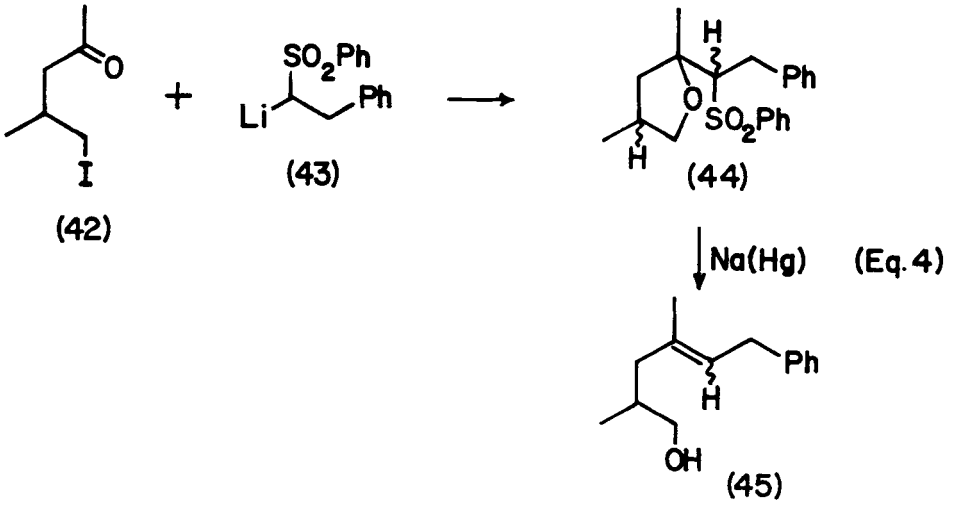


Scheme 6

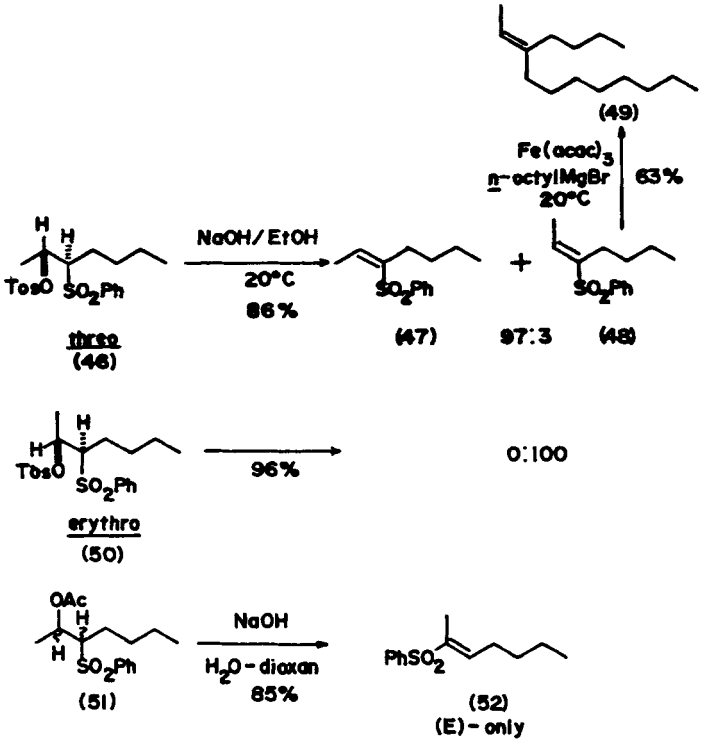
illustrated in Scheme 6. Addition of cyclohexanone to the sulphone anion (29) failed to give an intermediate (30) which could be acylated. Owing to an unfavourable equilibrium, (30) reverted back to starting materials - a problem which has plagued others[10,23].
However, by reversing the functionality of the fragments a stable adduct (33) was formed in which the less hindered secondary alkoxide was acylated and the product (34) reductively eliminated to olefin (35) in 54% overall yield. Tri-substituted olefins have been generated by reductive elimination of β-hydroxy sulphones (36) [15] and (39) [16] but retroaldolisation would probably complicate more hindered systems.

Trisubstituted Olefins

Unfortunately, there are not many applications of the Julia olefination to the synthesis of tri-substituted double bonds so no conclusions can be made about stereochemistry. The one case we have examined is not encouraging [24]. Reaction of the sulphone anion (43) (Eq. 4) with iodoketone (42) gave an alkoxide intermediate which underwent intramolecular alkylation to give a diastereomeric mixture of tetrahydrofurans (44). These were treated with a large excess of sodium amalgam in the usual way at room temperature to give the alcohol (45) as a 3:2 mixture of isomers.



More recently Julia and co-workers have developed a new sulphone-based stereocontrolled synthesis of tri-substituted olefins which consists of two key stereoselective reactions. First, treatment of the erythro and threo ß-tosyloxy sulphones (46 and 5o respectively) with sodium hydroxide in EtOH gave highly stereoselective anti-elimination reactions to the corresponding (Z) and (E) α,β-unsaturated sulphones (47) and (48) [25] (Scheme 7). Secondly, substitution of the sulphone group by a primary alkyl group was effected [26] by reacting the α,β-unsaturated sulphone with a Grignard reagent in the presence of 1 mole % of $Fe(acac)_3$. As can be seen from the example shown in Scheme 7 the substitution occurs with retention of configuration. The potential of this sequence was enhanced by the discovery that both the erythro and threo β-acetoxy sulphones (51) underwent a stereo-convergent β-elimination to the (E) α,β-unsaturated sulphone (52) exclusively in the presence of sodium hydroxyde in dioxan.

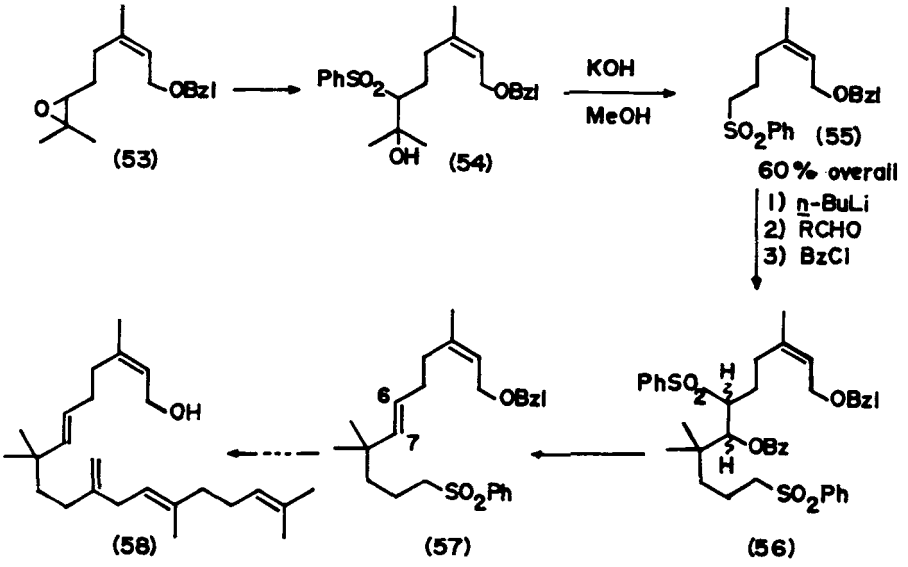


Scheme 7

The Synthesis of Moenocinol and Diumycinol

The sulphone group is conspicuous for its premier strategic role in our recent syntheses of the antibiotic fragments moenocinol (58)[27] and diumcynol (67)[28] in which every C-C bond-forming reaction exploited the nucleophilic properties of sulphone-stabilised carbanions or the ability of a sulphone to serve as a leaving group under specific and well-defined conditions. In particular, the virtues of the Julia olefination were used to good account.

The retroaldolisation of β-hydroxy sulphones which hitherto has been treated as a nuisance was turned to our advantage in the cleavage of the terminal three carbons of nerol benzyl ether (53) (Scheme 8). Thus nucleophilic cleavage of the oxiran function in (53) by sodium thio-



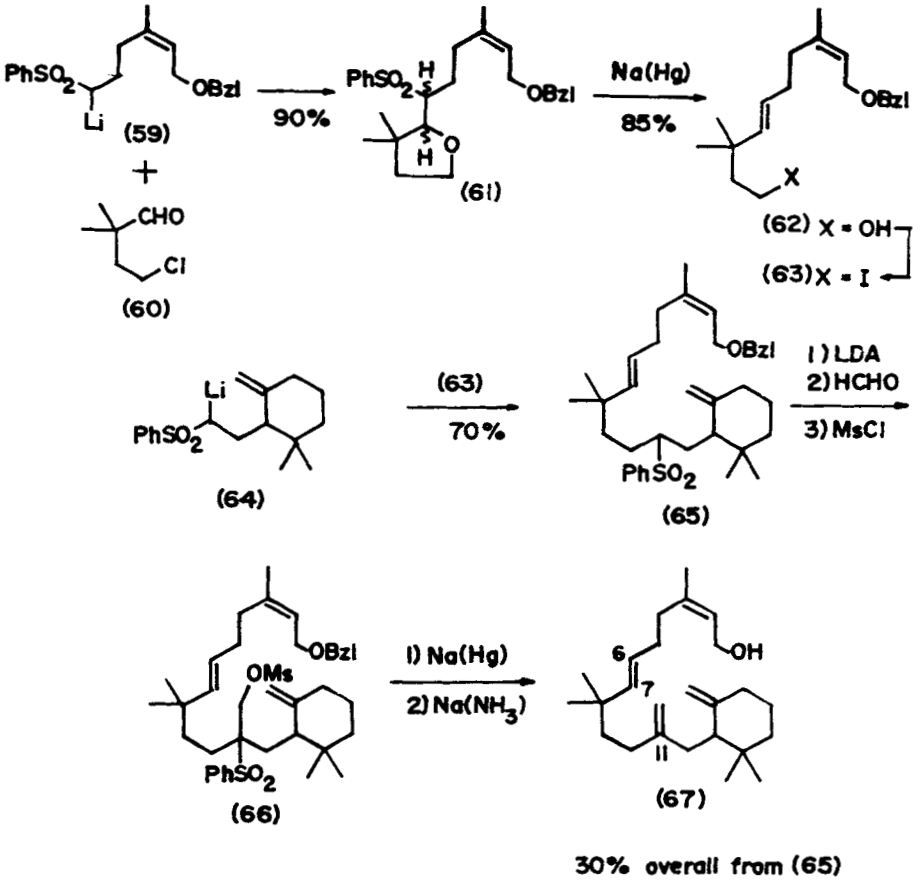
Scheme 8

phenoxide gave a thioether which was oxidised to the β-hydroxy sulphone (54). By warming (54) in a solution of potassium hydroxide in methanol the retroaldol reaction occurred smoothly to give the desired sulphone (55) in 60% overall yield from (53). The C_6-C_7 trans double bond was introduced in 54% overall yield as shown in Scheme 8. The high stereoselectivity of the Julia olefination is noteworthy because previous attempts to introduce the C_6-C_7 double bond by means of the Wittig reaction gave only the cis olefin. Similarly, attempts to use other reductive elimination reaction procedures also failed to secure a stereoselective synthesis of the desired olefin [29]. It is also noteworthy that the isolated sulphone function in (56) was not touched under the reac-

tion conditions.

Similar goals and strategies were used in our synthesis of diumycinol (67)[28] (Scheme 9). A slightly different tactic however was employed to introduce the trans double bond at C_6-C_7.

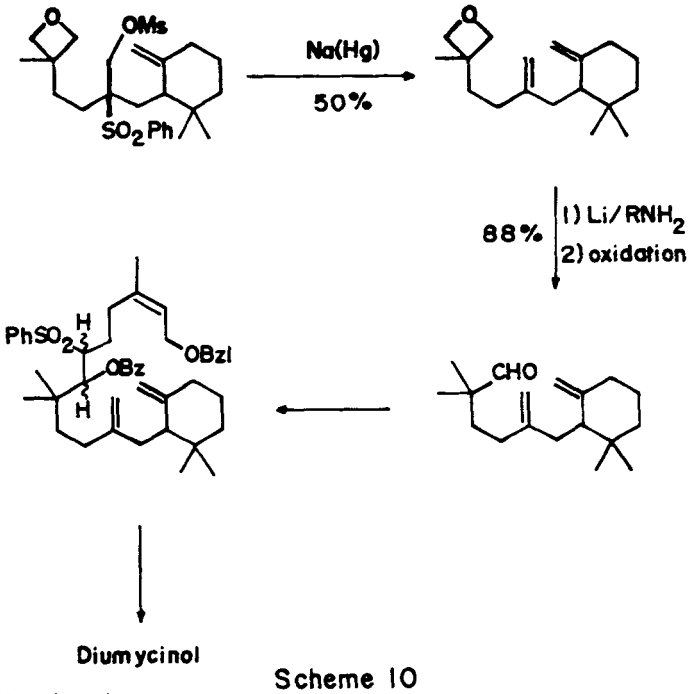
Stages 2 and 3 of the Julia olefination were combined in a single step to give the diastereomeric mixture of adducts 61 which gave the olefin 62 in 85% yield on treatment with sodium amalgam. Contraining the oxygen in a ring did not have an adverse effect on the anticipated high trans-stereoselectivity. The sketelon of di-



Scheme 9

umycinol was then completed in two stages involving alkylation of the sulphone carbanion (64) followed by a Julia ilefination to introduce the methylene group at C_{11}.

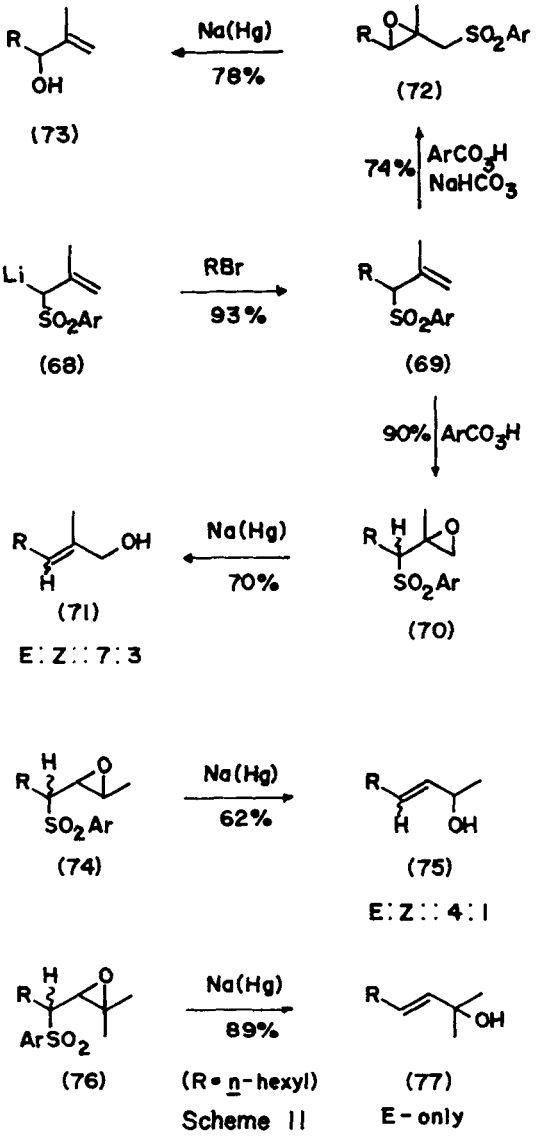
In an alternative approach to diumycinol, the double bonds at C_{11} and C_6 were introduced in reverse order by means of Julia olefinations shown in Scheme 10.



Scheme 10

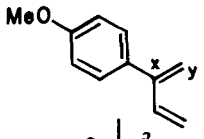
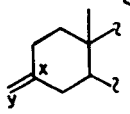
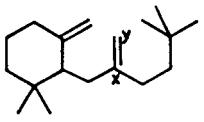
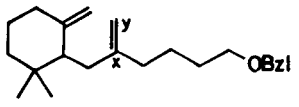
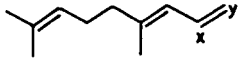
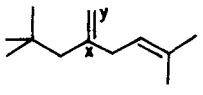
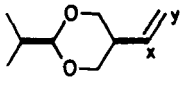
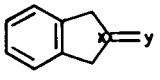
Useful Variations

The basic theme of the Julia olefination should be amenable to some synthetically useful variations. For example, we have devised a three-stage synthesis of allylic alcohols (Scheme 11) [30] consisting of 1) alkylation of a sulphone-stabilised allylic carbanion (68 → 69); 2) peracid oxidation of the allylic sulphone to a β,γ-epoxysulphone (69 → 70) and 3) reductive elimination of the β,γ-epoxysulphone to an allylic alcohol 70 → 71). The overall strategy is similar to that of the Evans-Mislow allylic alcohol synthesis based on allylic sulphoxides [31].



Scheme II

TABLE 3

Entry	Olefin[a]	Yield (%)[b]
1		77[c]
2		68[c]
3		31[d]
4		71[d]
5		80[d]
6		75[d]
7		50[d]
8		71[e]

[a] x and y represent the site of the phenylsulphonyl and trimethylsilyl groups respectively in the β-silylsulphone.

[b] Overall yield from the sulphone and iodomethyltrimethylsilane.

[c] Reference

[d] Unpublished work of P. Kocienski, M. Todd, and G.S. Cockerill

[e] K. J. McCullough, Tetrahedron Lett., 1982, 23, 2223.

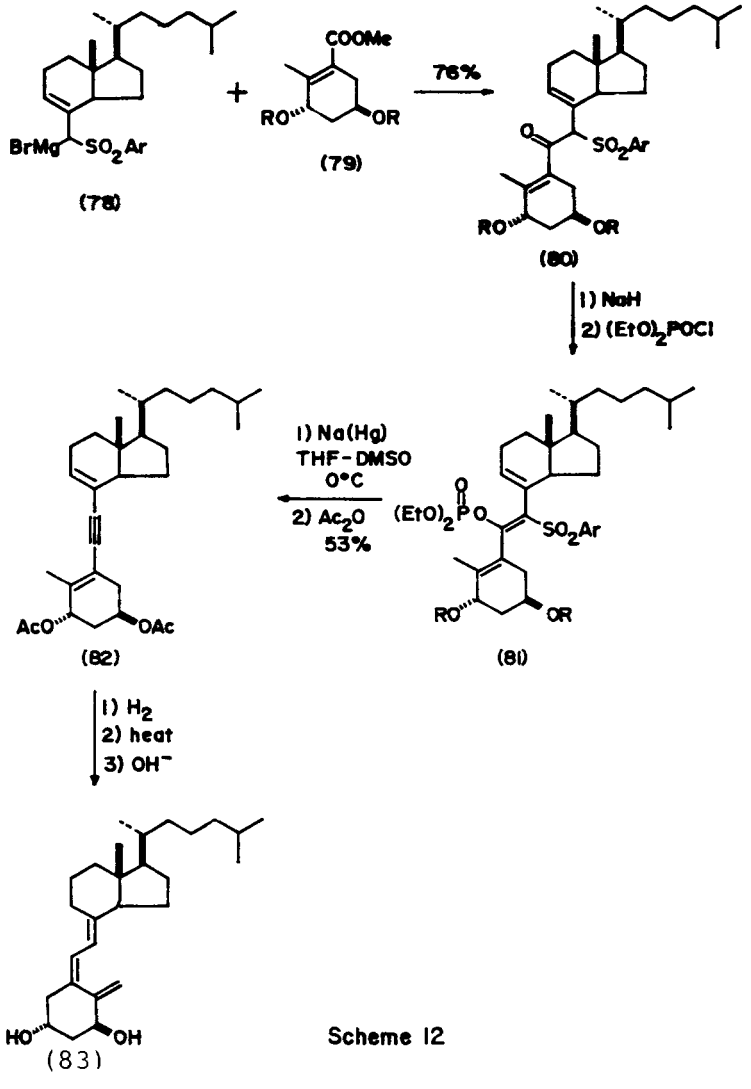
However, there are regiochemical advantages to the sulphone-based method exemplified by comparing the alkylation (68→69) (n-hexyl bromide, 96% yield, exclusively α) with the corresponding sulphoxide (n-hexyl iodide, 42% yield, α : γ = 2 : 5)[32].

A disadvantage of this procedure is that reductive cleavage of epoxysulphones leading to tri-substituted double bonds is not stereospecific. Furthermore, the stereochemistry of the product depends on the stereochemistry of the β,γ-epoxysulphone. Thus, reductive elimination of the major (crystalline) and minor diastereoisomers of (70) gave the allylic alcohols 71 in 73% yield (E : Z = 5 : 1) and 62% yield (E : Z = 2 : 1) respectively. In the case of the α-branched disubstituted allylic alcohol (77), only the (E)-isomer was obtained from the diastereomeric mixture (76).

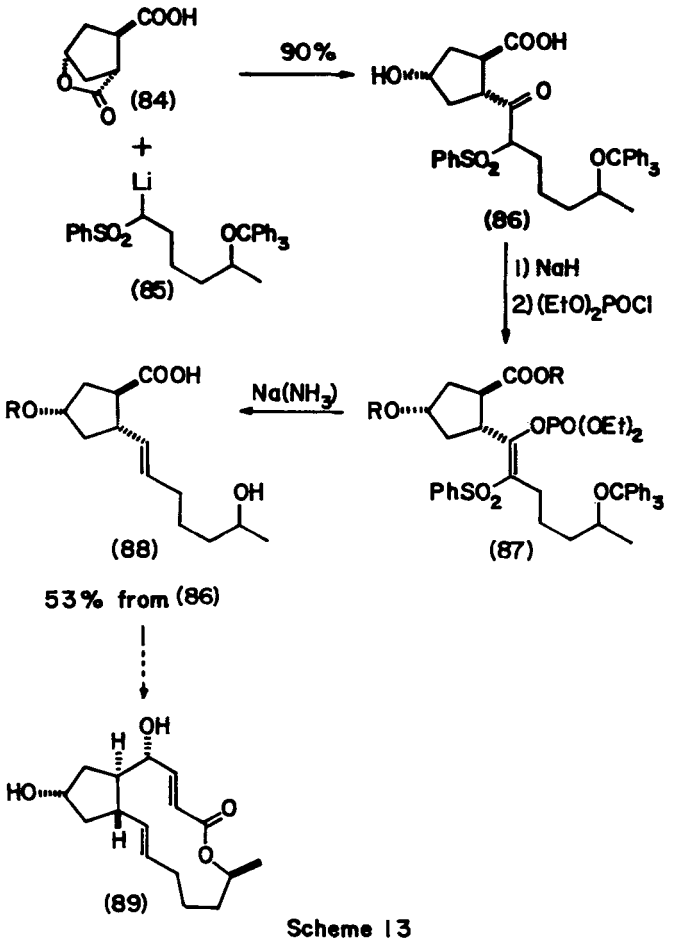
The scope of the sulphone-based allylic alcohol synthesis was recently enhanced by the discovery of a 1,3-rearrangement of allylic sulphones [33] caused by m-chloroperbenzoic acid and sodium hydrogen carbonate in aqueous dichloromethane. For example, reaction of (69) with 1.25 equivalents of the peracid and 2.5 equivalents of sodium hydrogen carbonate in a rapidly stirred mixture of water and dichloromethane at $0^{\circ}C$ gave epoxysulphone (72) in 79% yield uncontaminated by (70). Reductive elimination of (72) gave allylic alcohol (73) in 78% yield. A radical chain mechanism was proposed for the rearrangement which is restricted to those allylic sulphones in which the arylsulphonyl group can migrate from a more- to a less-substituted carbon. Lin and Whitham [34] have recently demonstrated alternative conditions for effecting a similar rearrangement.

A connective synthesis of acetylenes inspired by the

Julia olefination was developed by Lythgoe and co-workers [35] for the synthesis of 1α-hydroxyvitamin D_3 (83) [36,37] as shown in Scheme 12. The β-oxo sulphone (80) derived by condensation of allylic sulphone (78) and ester (79) was converted to the enol phosphate (81)



Scheme 12



Scheme 13

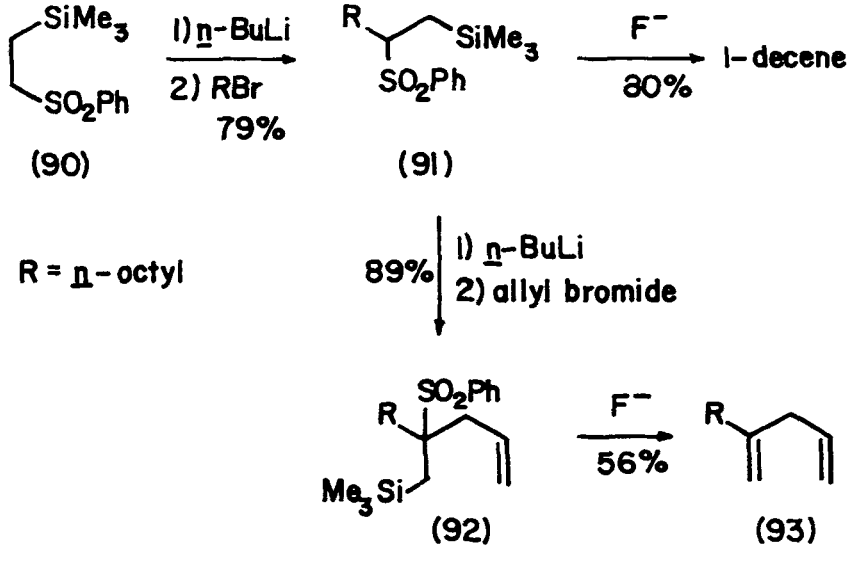
reductive elimination of which gave en-yn-ene 82. A similar procedure was developed simultaneously by Bartlett [38].

The precise conditions for the reductive elimination are important. Use of sodium amalgam in THF-MeOH or THF alone gave messy reactions owing to substantial cleavage of the P-O bond of the enol phosphates. Use of sodium in liquid ammonia can be controlled to give acetylenes in good yield with very little over-reduction to the trans-olefin [38]. However, the use of sodium amalgam in THF-dimethyl sulphoxide is particularly convenient

and over-reduction is not a problem even with conjugated en-yn-enes such as (82). A deliberate over-reduction was used by Bartlett and Green [39] as a key step in a synthesis of the trans olefin (88) which was an intermediate in a synthesis of brefeldin (89) (Scheme 13). A related connective synthesis of acetylenes based on the reductive elimination of β-triphenylphosphonium enol triflates has recently been reported [40].

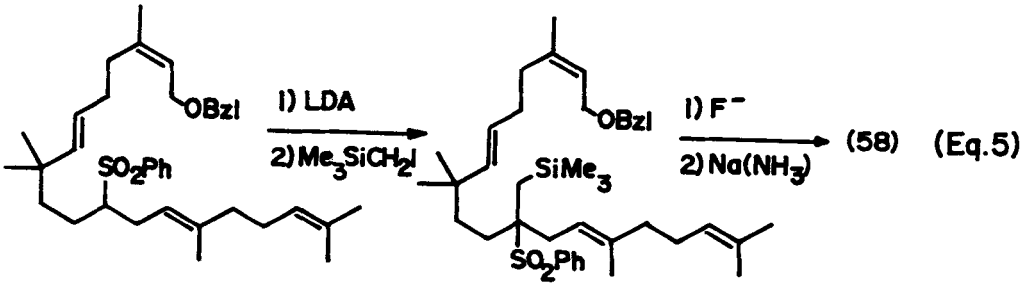
β-Silyl Sulphone Elimination

The fluoride-induced elimination of β-trimethylsilyl sulphones to give terminal olefins was first reported in 1979 [41]. The β-silyl sulphone (91), prepared by alkylation of the lithio derivative of (90) (Scheme 14), gave 1-decene on refluxing in THF with 1.5 eq. of n-$Bu_4NF.3\ H_2O$ for one hour. Similarly, a second alkylation gave (92) which was converted to (93) with fluoride. Thus the sulphone (90) may serve as a synthon for $CH_2{=}CH^-$ or $CH_2{=}C^-$

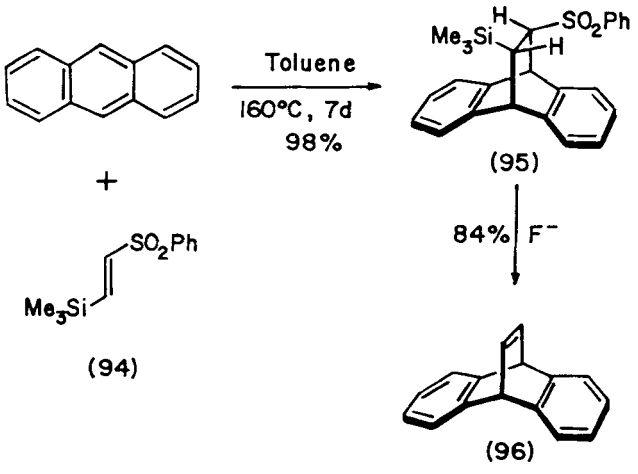


Scheme 14

in which the olefin is liberated under specific and mild conditions. These assets were exploited to introduce the C-11 methylene of moenocinol (Eq. 5) [27] and Table 3 lists some further examples in which the β-silyl sulphones were prepared by alkylation of the appropriate lithio sulphone by iodomethyltrimethylsilane.

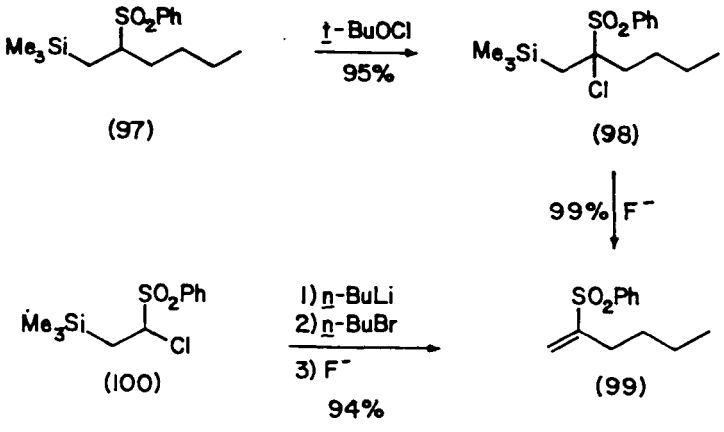


A major detraction to the β-silyl sulphone route to olefins is its narrow scope. With the exception of chloro- and iodotrimethylsilane there are no α-haloalkyl silanes commercially available and there are few synthetic routes to them. Nonetheless, a few adaptations of the basic idea have provided some synthetically useful methods. For example, the sulphone (94) has been employed as an acetylene equivalent in Diels-Alder reactions (Scheme 15) [43]. Since the initial adduct (95) could be alkylated, the dienophile (94) also served as a synthon for mono-substituted acetylenes.

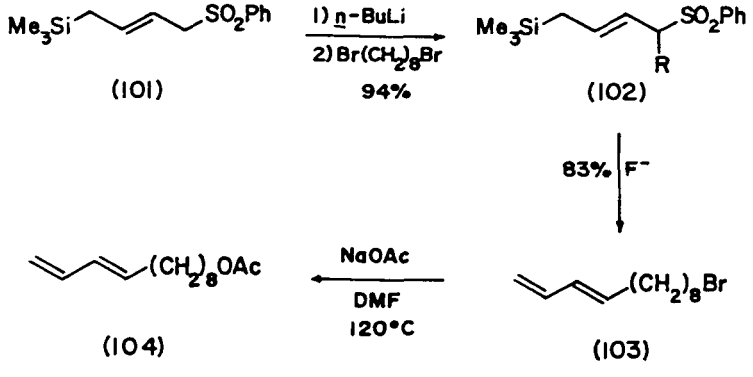


Scheme 15

Recently, Hsiao and Shechter have extended the fluoride-induced elimination method still further. The β-silyl sulphone (97) (Scheme 16) [44] underwent rapid chlorination with t-butyl hypochlorite to give the α-chloro sulphone (98). Subsequent treatment with fluoride effected elimination of the chloride preferentially to give the vinyl sulphone (99) in excellent overall yield. Alternatively, alkylation of the α-chloro sulphone (100) followed by fluoride-induced elimination gave (99) in good yield.



A new synthesis [45] of the red bollworm pheromone (104) (Scheme 17) has demonstrated the use of the (E)- and (Z)-1-benzenesulphonyl-4-trimethylsilyl-2-butenes (101) as an (E)-1-(1,3-butadienyl)synthon. The fluoride-induced 1,4-elimination of fluorotrimethylsilane and benzenesulphinate was stereoconvergent and gave only the desired (E) stereochemistry in (103).



Scheme 17

Conclusion

In this review I have tried to show that the Julia olefination is a valuable alternative to the Wittig reaction - especially for the stereoselective synthesis of trans-1,2-disubstituted olefins. Indeed, it has been successfully applied to complex natural product syntheses wherein the Wittig reaction proved infeasible. The β-silyl sulphone elimination, though much narrower in scope, has also proven useful and recent advances in analogous systems [46,47] suggests that it too is gaining adherents.

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