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RECENT PROGRESS ON REARRANGEMENTS OF SULFONES

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The present review surveys the main literature reports on rearrangements of sulfones published during the last decade. The report concentrates on the three most studied rearrangements, namely, 1,3-sulfonyl migration, Ramberg–Bäcklund rearrangement and pinacol-reduction rearrangement. Both mechanistic aspects and synthetic applications have been emphasized. The first type of rearrangements has been found to occur by both free radical as well as ionic mechanism. A number of synthetic applications, including intramolecular rearrangement–cyclization and regioselective alkene synthesis have been described. With regard to Ramberg–Bäcklund rearrangement, it is of special interest to note the novel isolation of previously postulated episulfone intermediate, and the renewed interest in this type of rearrangement as well as its various important modifications. Due to the novel developments a number of synthetic applications have been described, including preparation of various natural products, novel electrically conducting materials, and enediynes. The last rearrangement is of interest no only due to its mechanistic aspects, but also because it provides the possibility of ring enlargement of cyclic ketones.

Keywords: Pinacol-reduction rearrangement; Ramberg–Bäcklund rearrangement; sulfones; 1,3-sulfonyl migration

CONTENTS

* Corresponding author.

1. INTRODUCTION

The present review surveys the major developments on the subject of sulfone rearrangements, which have been published since the publication of the Patai chapter on this subject some ten years ago.[1] However, unlike the former, which dealt with rearrangements involving sulfones, we have now concentrated on rearrangements of sulfones only. That is only those papers dealing with rearrangements of sulfones directly have been included. However, we had to be rather selective in our choice due to space limitation. We therefore, apologize to those researchers whose studies were not included.

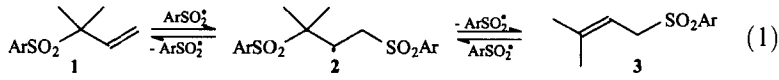
2. 1,3-ALLYLIC SULFONYL MIGRATION

2.1. Mechanistic Aspects of 1,3-Sulfonyl Migration

The 1,3-rearrangement of allylic sulfones has received considerable attention due to its synthetic and mechanistic interest beginning since its first experimental observation by Darwish and Braverman more than three decades ago.[2] Both ion pair[2–4] and free-radical chain

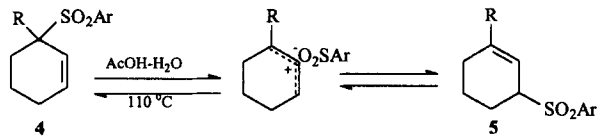
addition–elimination[5–7] mechanisms were suggested for 1,3-allylic sulfonyl migrations.

During the last decade the study of this rearrangement has been continued and extended. For example, Whitham and coworkers have described[8] the 1,3-rearrangement of α-substituted acyclic and cyclic allylic aryl sulfones under standard radical conditions: dibenzoyl peroxide (BPO)-CCl_4. In general, the more substituted double bond (more stable) isomer predominated and E/Z isomeric mixtures were obtained. Thus, α,α-dimethylallyl *p*-tolyl sulfone **1** readily rearranged to prenyl sulfone **3** under standard radical conditions, Eq. (1). A radical chain addition–elimination mechanism, involving as propagating step, sulfonyl radical addition to the double bond of the allylic sulfone followed by β-scission of the resulting arenesulfonyl radical **2**, was proposed.



(1)

It is interesting to note that similarly substituted cyclic allylic sulfones such as 1-alkylcyclohex-2-enyl *p*-tolyl sulfones **4** rearranged only sluggishly under radical conditions but underwent smooth isomerization on heating in AcOH–H_2O (3:2) at 110 °C, Eq. (2). This isomerization was not inhibited by hydroquinone. Therefore, a dissociation–recombination mechanism, involving an ion pair has been suggested. The ion pair is presumed to be fairly "intimate" since solvolysis products were not observed.

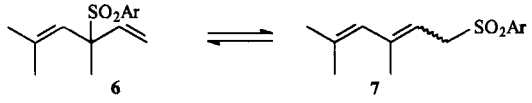


(2)

Further evidence supporting the ion-pair mechanism for the substituted cyclohexenyl sulfones emerged from an investigation of *t*-butyl sulfones. 1-Methylcyclohex-2-enyl *t*-butyl sulfone was converted to its allylic isomer even under milder ionization conditions than those required for the *p*-tolyl analog. On the other hand, α,α-dimethylallyl *p*-tolyl sulfone undergoes a much more rapid rearrangement under radical conditions than the corresponding *t*-butyl sulfone. This result could be explained by two different mechanisms. One

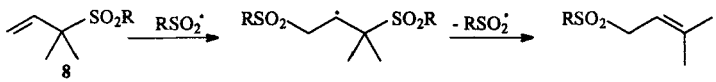
possibility for higher reactivity of the *t*-butyl sulfone towards dissociation–recombination is that it is a ground state effect whereby the greater steric demand of the *t*-butyl sulfonyl group compared to that of the arenesulfonyl group leads to steric acceleration of ionization.

In general, some extra cation stabilizing influence is needed to promote the ionization mechanism. For example, additional carbocation stabilizing substituents such as 1-alkylcyclohexenyl,[8] methylthio[9] or phenylthio[3] can facilitate an ion-pair mechanism for the 1,3-rearrangement. A vinyl substituent can operate in the same way.[8] Thus the bis-allyl sulfone **6** rearranged to the dienyl sulfone **7** on heating in aqueous acetic acid, Eq. (3).



6 **7** (3)

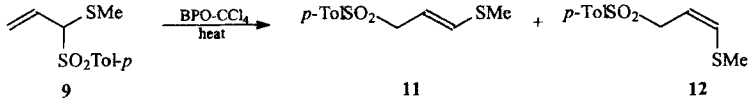
A radical chain addition–elimination mechanism, Eq. (4), has also been suggested for the 1,3-rearrangement of the allylic alkyl sulfones **8**.[10] In this case, carbon tetrachloride was unsatisfactory as solvent for the BPO-induced rearrangement due to competing abstraction from the solvent and S_H2' substitution of the sulfone by the resulting Cl_3C radical. However, the rearrangement proceeded satisfactory on treatment with BPO in *t*-BuOH, or with $MeSO_2Na$ in aqueous AcOH. The latter set of conditions was also shown[8] to favor a free-radical mechanism. Sulfinic acids behave as an alternative source of $ArSO_2$ radicals thereby establishing the same propagating steps involving **2** proposed for the BPO-CCl_4 conditions. This was established by the fact that sodium *p*-toluenesulfinate in the absence of acid did not act as an effective catalyst and inhibition by hydroquinone had been detected.[8] The rearrangement was very slow (R = *t*-Bu) or altogether unsuccessful (R = CH_2Ph, CH_2COMe) in cases where the intermediate sulfonyl radical could undergo loss of sulfur dioxide to give a resonance-stabilized alkyl radical.



8 (4)

R = Me, Et, *i*-Pr, *t*-Bu, CH_2SiMe_3, $CH_2CH_2SiMe_3$ $CH_2CH(OH)Me$

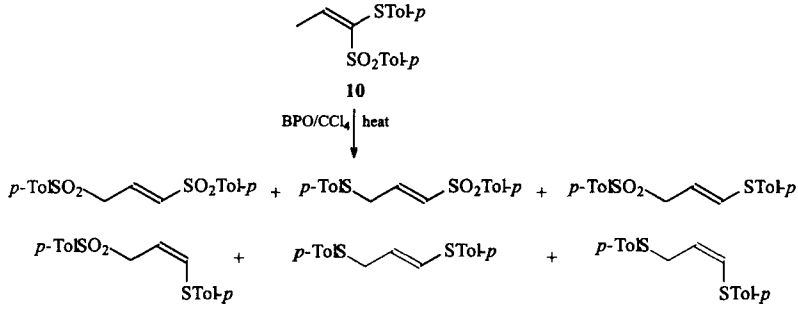
In continuation, the α-alkylthio and α-arylthio substituted allylic sulfones **9** and **10**, respectively, were investigated under free radical rearrangement conditions.[11] The sulfonyl sulfide **9** was completely rearranged to a mixture of the *E*- and *Z*-methylthioallyl *p*-tolyl sulfones **11** and **12** with a ratio of *E* to *Z* isomers $\sim 2:1$, Eq. (5). It thus appears that rearrangement of **9** under radical conditions occurs by a clean 1,3-shift of the *p*-tolylsulfonyl group involving addition–elimination of a *p*-TolSO$_2$ radical. However, since it is known[12] that 3-alkylthioprop-1-enyl *p*-tolyl sulfones are thermodynamically less stable than their vinyl sulfide isomers such as **11** and **12** and are readily isomerized to them under mildly basic conditions, the possibility exists of rearrangement by a competing 1,3-shift of the methylthio group followed by a 1,3-prototropic shift. The latter possibility was excluded by an experiment in which α-deuterated **9** was subjected to the rearrangement conditions and gave **11** and **12** containing deuterium only in the α-positions to the thiomethyl substituent. Therefore, the radical-induced rearrangement of **9** involves preferential migration of the *p*-toluenesulfonyl group.



9 **11** **12**

(5)

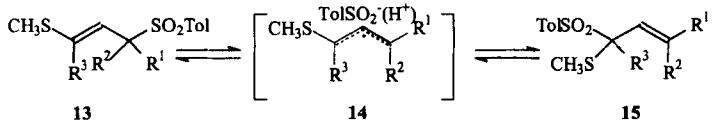
In contrast to the sulfone **9**, the *p*-tolylthio substituted sulfone **10** under analogous rearrangement conditions gave a more complex set of products corresponding to those expected for migration of both *p*-tolylthio and *p*-toluenesulfonyl groups, Eq. (6).



(6)

It follows from the nature of the products and the reaction conditions that the reaction occurs by addition–elimination involving both *p*-TolS$^{\bullet}$ and *p*-TolSO$_2^{\bullet}$ radicals. It seems likely that the main reason for the difference between the outcome of the rearrangement of the methylthio substituted sulfone **9** and of the *p*-tolylthio substituted sulfone **10** is the nearly 700 fold greater leaving group ability of ArylS$^{\bullet}$ *vs.* AlkylS$^{\bullet}$ from the relevant β-thio substituted radical.[13]

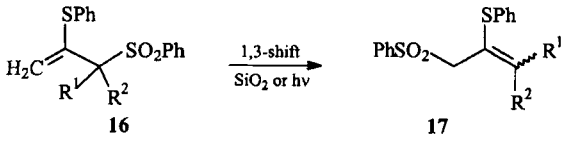
Contrary to the α-methylthio substituted allylic sulfones **9**[11] an ion-pair mechanism was proposed for the SiO_2-catalyzed reversible 1,3-rearrangement of the γ-sulfenylated allylic system **13**, Eq. (7).[9]



13 **14** **15** (7)

Since protic acids such as *p*-toluenesulfonic or acetic acid exhibit a catalytic activity for this rearrangement, it may be suggested that the present rearrangement occurs *via* a cationic intermediate **14**. The position of the SiO_2-catalyzed equilibrium between **13** and **15** was strongly influenced by the number and position of the alkyl substituents. The equilibrium lies to the side of **15** when the position α to the sulfonyl group in **13** is dialkylated ($R^1 = R^2 = Et$, *n*-Pr, *n*-Bu, $PhCH_2$); in contrast, monoalkylated **13** (R^1 = alkyl, $R^2 = H$) apparently do not undergo the allylic 1,3-rearrangement. This is accounted for in terms of the stabilizing effect of a methylthio group on an adjacent C=C bond to allow exclusive production of the thermodynamically more stable **13** at equilibrium with **15**. Alkyl substituents facilitate the rearrangement by stabilization of the transient cation **14**. The 1,3-rearrangement of methylthio substituted allylic sulfones **13** *via* the ion pair mechanism[9] again supports the influence of carbocation stabilizing substituents on the promotion of an ionization mechanism.[3,8]

Padwa and coworkers[14,15] have investigated the behavior of β-phenylthio substituted mono and dialkylated allylic sulfones **16** in terms of 1,3-allylic sulfonyl migration under two sets of conditions, namely, ionization and free radical, Eq. (8). The first was to subject the allyl sulfone to silica gel chromatography, and the second to heat the sulfone at 80 °C in solution with exposure to light.

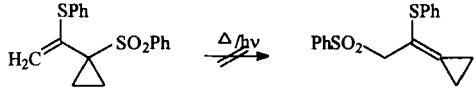


16 17 (8)

R^1, R^2 = alkyl, allyl, benzyl

Two different paths can be put forth regarding the mechanism of this rearrangement. One route includes a fairly tight ion-pair mechanism, which is probably applicable to the silica gel-induced rearrangement.[9] The alternative path occurs in solution and involves a radical chain mechanism. The heat and/or light initiate the reaction by bringing about cleavage of the allyl-sulfone group bond. The benzenesulfonyl radical so produced adds to the double bond of another molecule, leading to a new radical which loses the resident benzenesulfonyl group to generate the rearranged isomer. In all cases the thermodynamically more stable alkene with the more substituted double bond is the exclusive product, and *E*/*Z* isomeric mixtures are obtained. This mechanism is in full agreement with the results of Whitham.[8,10,11]

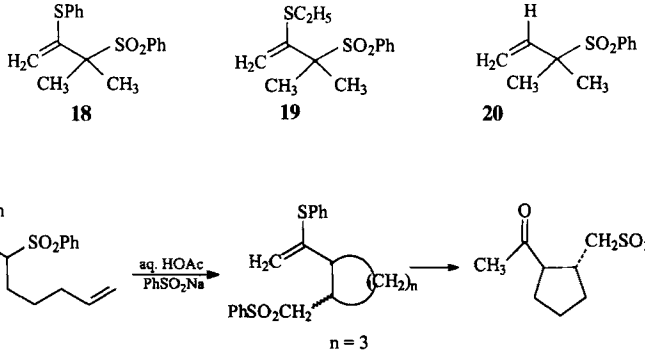
The free radical addition-elimination mechanism has received further support through the following results.[15] Polar solvents, such as acetonitrile and dimethyl sulfoxide, did not increase the rate of rearrangement. On the other hand, a catalytic amount of hydroquinone, a known free-radical inhibitor, completely suppressed the reaction. It is interesting to note that the rearrangement did not occur in the case of cyclopropyl substituted sulfone, Eq. (9). This can be readily rationalized since methylenecyclopropanes are known to be thermodynamically less stable than vinyl substituted cyclopropanes.[16]



(9)

The effect of the nature of substituents at the β-position was also investigated. The presence of a phenylthio group in **18** or of an ethylthio group in **19** groups accelerates the reaction by 2 orders of magnitude *vs.* the unsubstituted sulfone **20**. This result is expected for a mechanism involving addition of the electrophilic $PhSO_2^{\bullet}$ radical to the more electron-rich π-bond.

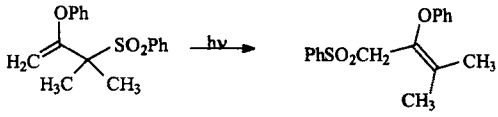
In those cases, where 2-phenylthio substituted allylic sulfones have an alkenyl side chain C–S cleavage is followed by cyclization of the allylic radical to give both five- and six-membered rings, Eq. (10).



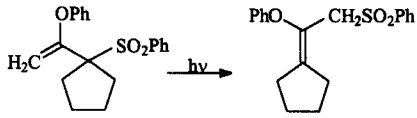
(10)

It is interesting to note that a rearranged sulfone was obtained under typical radical conditions as well as on heating in 60% aqueous acetic acid. A number of substituted acyclic allylic sulfones have been found to undergo 1,3-rearrangement under such conditions[7–9,17] and an ion pair dissociation-recombination mechanism has been proposed for these cases.

Just as phenylthio substituted allylic sulfones[14,15] alkoxy substituted derivatives underwent 1,3-sulfonyl rearrangement, Eqs. (11) and (12), *via* a radical chain mechanism.[18] A 1,3-sulfonyl shift occurred in quantitative yield under irradiation with 300 nm light.



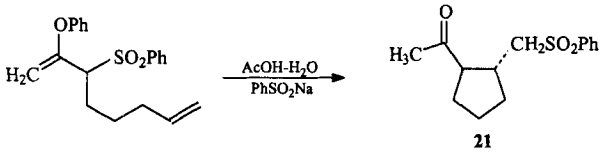
(11)



(12)

2.2. *Tandem Rearrangement Cyclization Reactions of Allylic Sulfones*

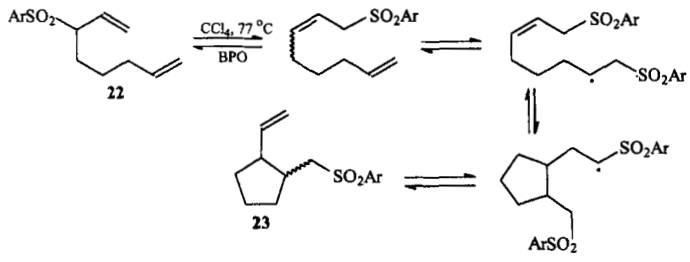
Some efforts were made[18] to use this radical-induced 1,3-rearrangement of 2-phenoxy substituted allylic sulfones to promote intramolecular 5-exo cyclization reactions. However, all attempts to effect such a cyclization under a variety of typical radical conditions were unsuccessful. On the contrary, an allylic sulfone cyclization was found to proceed upon heating with sodium benzenesulfinate in aqueous acetic acid, Eq. (13). It seems quite possible that the reaction proceeds via a tight ion pair which ultimately produces the keto sulfone **21**.



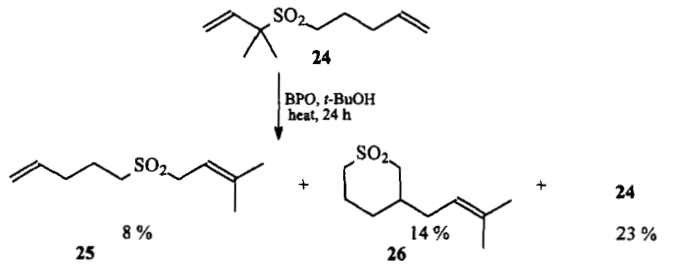
21 (13)

On the other hand, Whitham[8,10] presented some evidence in favor of a radical mechanism of the 1,3-sulfonyl migration using sodium *p*-toluenesulfinate in aqueous acetic acid. Therefore, the interpretation of these results still remains to be completed.

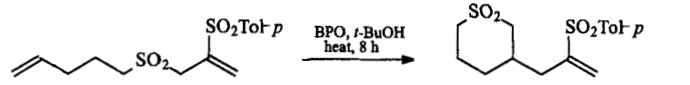
The 1,3-sulfonyl migration of unsaturated allylic sulfones has also been used in a "one-pot" rearrangement–cyclization to obtain cyclic sulfones.[10,19] Thus, an allylic sulfone such as **22** readily gave a cyclized product **23** with the yield > 90%, since the ring closure step corresponds to the formation of a 5-membered ring from a hex-5-enyl radical, Eq. (14). This reaction was considered to occur by a radical chain mechanism.[19] 4-Pentenyl sulfones[10] were obvious substrates for this rearrangement–cyclization sequence, since cyclization of the intermediate 4-pentenesulfonyl radical might occur, leading to a cyclic product. However, the 4-pentenyl sulfone **24** was rather resistant to rearrangement–cyclization and gave only a mixture of the acyclic 1,3-rearranged sulfone **25**, the cyclic sulfone **26**, and recovered starting **24**, Eq. (15).[10] This result may be rationalized in terms of the electronic nature of the radicals involved. However, the formation of the cyclic sulfone was promoted by incorporating an electron-withdrawing group at the β-position of the allylic sulfone, in order to increase the efficiency of the capture of the nucleophilic cyclized radical, Eq. (16).



(14)



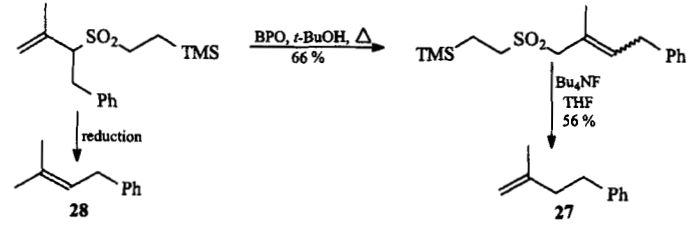
(15)



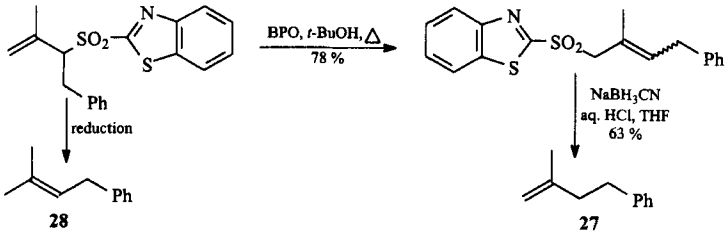
(16)

2.3. Synthetic Application of 1,3-Allylic Sulfonyl Migration

The 1,3-rearrangements of allylic sulfones may be a useful tool in organic synthesis since the activating sulfonyl group is transferred from one end to the other end of the allylic system. Radical-induced 1,3-rearrangement of appropriately substituted allylic sulfones in conjunction with reductive desulfonylation has been successfully used for a regioselective alkene synthesis, Eqs. (17) and (18).[20] The same sulfone was a precursor of either the isopropenyl **27** (*via* 1,3-sulfonyl rearrangement) or the isopropylidene **28** (by direct reduction) isomeric products.

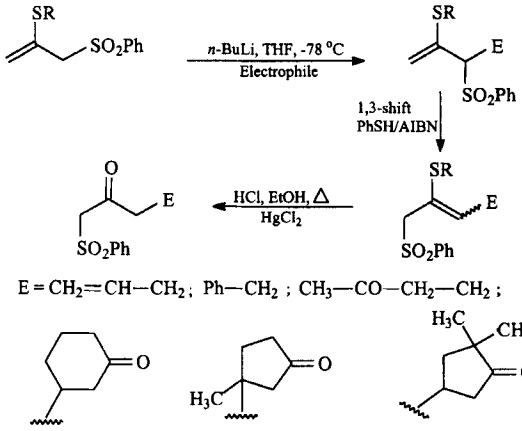


(17)



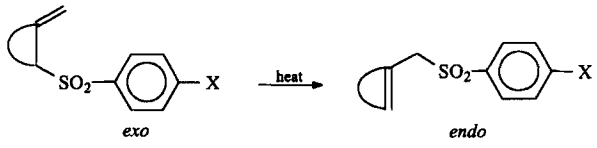
(18)

In an another application, the 1,3-rearrangement of β-thio substituted allylic sulfones has been used as a sulfoacetonylation tool for the conversion of enones into diketo sulfones, which then leads to bicyclic alkanediones, Eq. (19).[21] A free-radical chain transfer mechanism has been suggested for this thiol-AIBN induced rearrangement.



(19)

An interesting example of 1,3-sulfonyl migration has been described by Roy and coworkers.[22] *exo*-Methylenecycloalkyl sulfones, obtained by photostimulated reactions of cycloalkyl cobaloximes with arenesulfonyl halides, undergo facile 1,3-allylic rearrangement to *endo*-isomers, Eq. (20).



(20)

On the basis of mechanistic and theoretical studies this rearrangement is proposed to involve a [1,3]-sigmatropic migration of the sulfonyl group. This was the first example of a 1,3-sulfur shift in allylic sulfones wherein the allylic migration takes place from an *exo*- to an *endo*-cyclic framework.

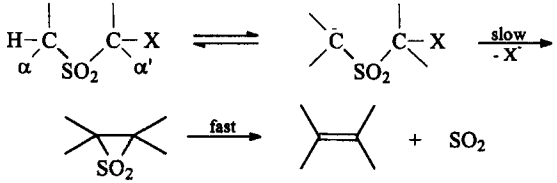
The following results support the proposed mechanism. The rearrangement is temperature dependent; no rearrangement takes place upon irradiation at low temperature; a similar product distribution is observed for reactions conducted in the dark, in diffused light and in the presence of one molecular equivalent of hydroquinone.

3. THE RAMBERG–BÄCKLUND REARRANGEMENT

The Ramberg–Bäcklund rearrangement[23] of halo sulfones in the presence of base, leading to olefin with accompanying loss of hydrogen halide and sulfur dioxide is one of the most important reactions of sulfones in general and is of both synthetic and mechanistic interest. A number of excellent reviews have been published during the last two decades.[1,24–26] Consequently, we shall concentrate on the latest developments in this area.

3.1. Mechanism of the Ramberg–Bäcklund Rearrangement: Isolation of Episulfones

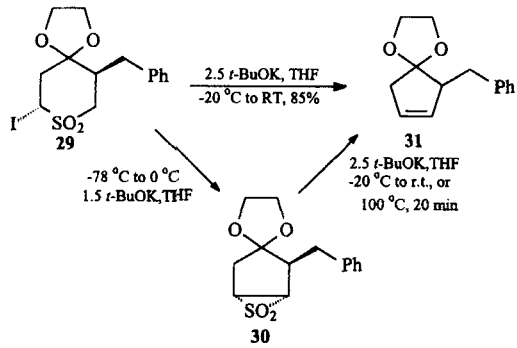
The general mechanism of the Ramberg–Bäcklund rearrangement is shown in Eq. (21). It has been established[24,27] that the second step, involving 1,3-displacement of the halide ion by the carbanion and formation of an episulfone, is rate determining, and the stereochemistry of the resulting olefin is established during this step.



(21)

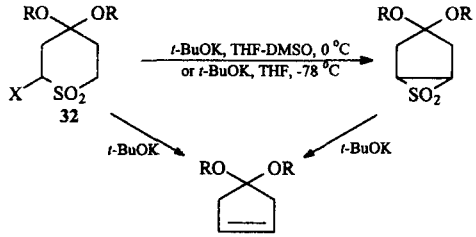
Until recently, the postulated episulfone intermediate could not be isolated under usual rearrangement conditions. Only in the year 1989 Taylor and coworkers[28] reported the first example of an isolable episulfone obtained by treatment of an α-halo sulfone with base. This

was made possible by the facile low-temperature Ramberg–Bäcklund rearrangement of a 2-iodothiane dioxide, Eq. (22). Treatment of **29** with 2.5 equivalents of *t*-BuOK in THF at −20 °C, followed by warming to room temperature, produced the expected cyclopentene **31** in 85% yield. When the reaction was carried out at −78–0 °C with 1.2 equivalents of *t*-BuOK, however, **31** was the minor product, the episulfone **30** being obtained as a white crystalline solid in 69% yield. Treatment of **30** with excess *t*-BuOK at −20 °C to room temperature gave **31** as the only observable product in 81% yield.



(22)

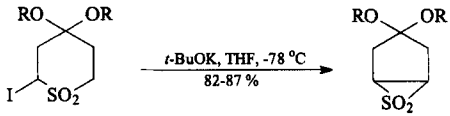
In continuation, it has been shown[29] that the presence of iodine as the leaving group is not strictly necessary; the α-chloro and α-bromo sulfones **32** (X = Cl, Br, I) also gave the corresponding episulfones in high yield on treatment with *t*-BuOK at low temperature, Eq. (23).



(23)

In a similar manner, the unsubstituted thian-4-one ketals **33** underwent a smooth conversion to the corresponding episulfones in high yield at −78 °C, Eq. (24). However, all attempts to prepare α-alkylated derivatives, i.e. compounds bearing substituents at the episulfone bridgehead position, were unsuccessful, although their Ramberg–Bäcklund rearrangement to cyclopentenes occurred efficiently. This suggested that the rate of loss of sulfur dioxide (either thermally

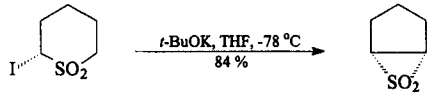
or in a base-promoted process) from a trisubstituted episulfone is fast compared with the disubstituted examples, allowing isolation of the latter compounds from the basic reaction media.



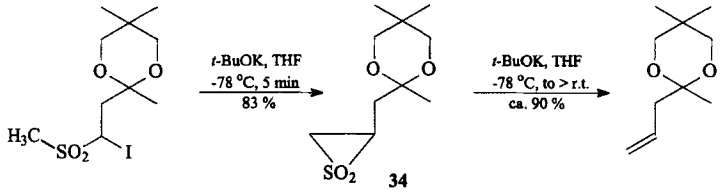
33 (24)

The presence of an acetal group at C-4 of the thian ring was not essential for episulfone stability, Eq. (25).[30] The importance of the ring size has also been investigated and it has been established that the 6-thiabicyclo[3.1.0]hexane 6,6-dioxide system is particularly favored. No trace of the expected episulfones was observed when seven-, five- or four-membered α-iodo sulfones were treated under the standard conditions for episulfone isolation.[30]

The scope of the procedure described above was extended and the first acyclic episulfone **34** was prepared by the Ramberg–Bäcklund rearrangement, Eq. (26).[30]



(25)

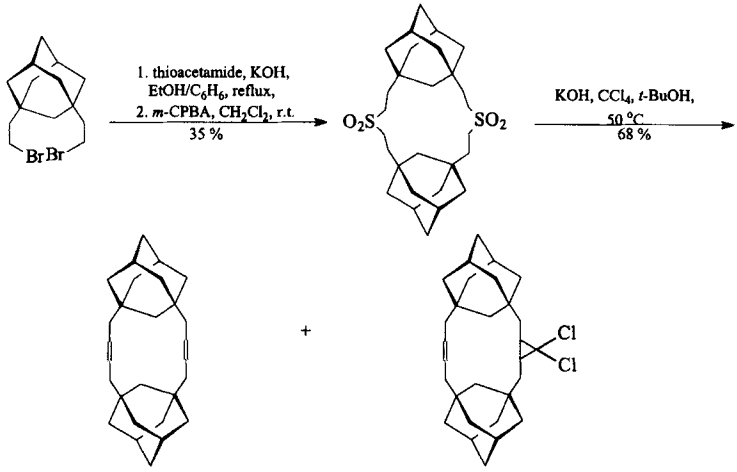


34 (26)

3.2. Some New Modifications of the Ramberg–Bäcklund Rearrangement

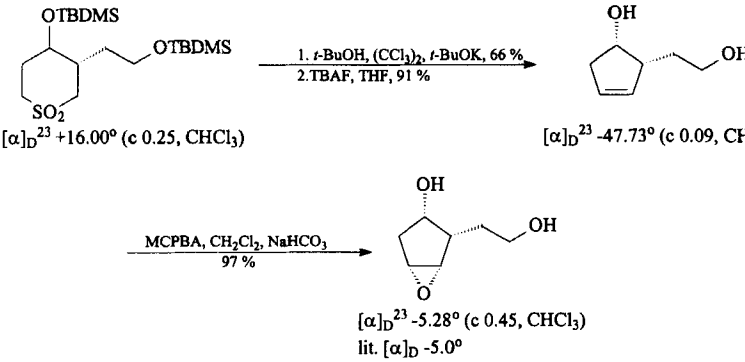
In recent years a number of modifications and extensions of the original Ramberg–Bäcklund rearrangement have been described. Since, usually, the preparation of α-halo sulfones is the most problematic stage in the Ramberg–Bäcklund strategy, the well-known Meyers procedure[31] represents a very attractive approach and had been used with considerable frequency in organic synthesis. It involves treatment of a sulfone possessing both α- and α'-hydrogens with potassium hydroxide

in carbon tetrachloride, which serves as the halogen source for *in situ* sulfone chlorination and, thus, allows to avoid the preparation of the α-halo sulfone in a separate step. This modification of the Ramberg–Bäcklund rearrangement was recently used for ring contraction and the synthesis of adamantanophanes,[32] Eq. (27).



(27)

The same protocol was used as a key step in the synthesis of prostaglandin synthons in optically pure form,[33] Eq. (28). Hexachloroethane, instead of carbon tetrachloride, was used as the chlorine source in this case.

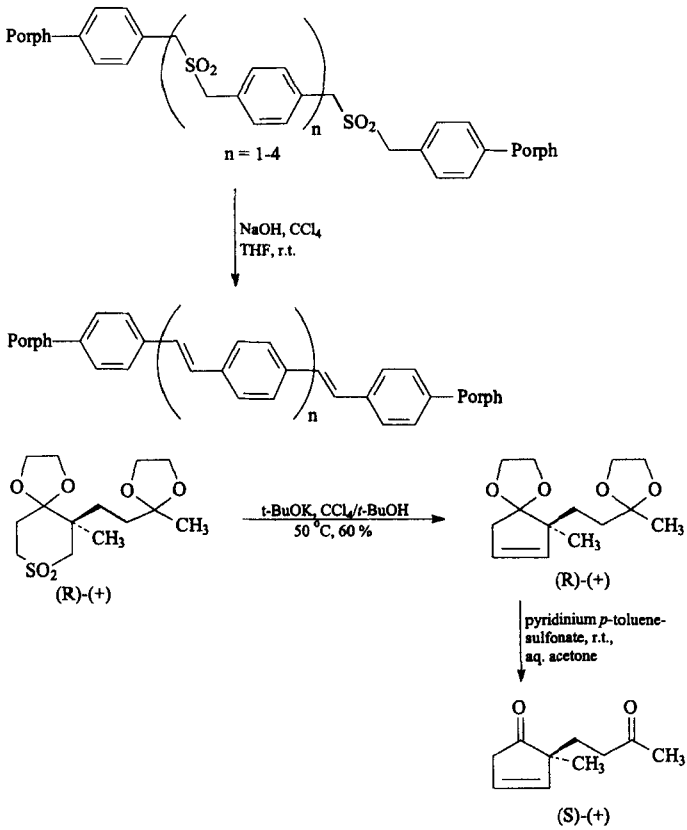


(28)

In another application, the Meyers modification of the Ramberg–Bäcklund rearrangement was the key step in the preparation of

oligo[phenylenevinylenes] terminated with porphyrins, novel electrically conducting materials, Eq. (29).[34] Ramberg–Bäcklund rearrangement allows a control of the conjugation length of phenylenevinylene oligomers, which is very important for organic semiconductors. Five double bonds were formed in one step, and they were all *trans*.

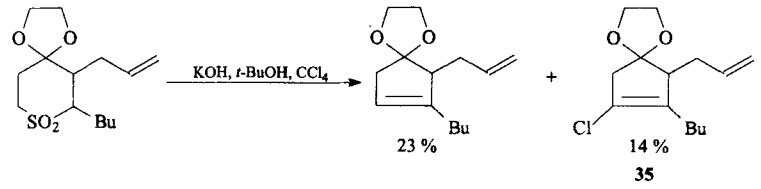
Matsuyama and coworkers[35,36] successfully employed a ring contraction approach through the Meyers modification of the Ramberg–Bäcklund rearrangement for the synthesis of some optically active cyclopentenones, Eq. (30).



(29)

(30)

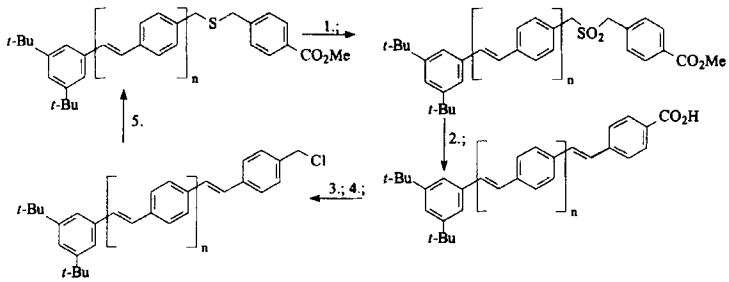
It is interesting to note that the same strategy was rather disappointing when applied to the synthesis of 2,3-disubstituted cyclopentenones because of the formation of the chlorinated by-product **35** together with the desired cyclopentene, Eq. (31).[37]



(31)

However, one should note some limitations in the applicability of the Meyers protocol to the synthesis of alkenes. This procedure works well with dibenzylic and benzhydryl alkyl type sulfones, whereas sulfones of other structural types may behave differently and yield complex mixtures of products.[38,39] The major disadvantage of the Meyers procedure is the formation of dichlorocarbene from CCl_4 under the basic reaction conditions and its addition to the alkene product. A further disadvantage is the dihalogenation of diprimary alkyl sulfones. Chan and coworkers [40] have suggested an improved version of the standard Meyers procedure, which involves replacement of carbon tetrachloride by CBr_2F_2 and of powdered KOH by alumina-supported KOH. With this reagent, $KOH/Al_2O_3–CBr_2F_2–t$-BuOH, the one-pot Ramberg–Bäcklund rearrangement proceeds smoothly with good yields and gives alkenes as the only product.

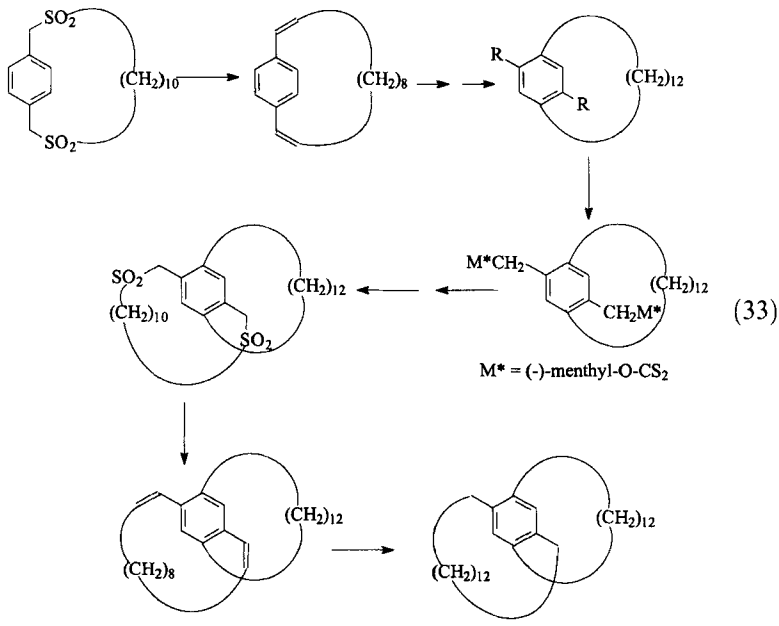
The above version of the Ramberg–Bäcklund rearrangement has been used for the stereoselective synthesis of oligo [(*p*-phenylene-(*E*)-vinylene)benzoic acids], the basic building block of novel electrically conducting materials, the oligo[phenylenevinylenes], Eq. (32),[41] as well as for the synthesis of various optically active (*m*)(*n*)paracyclophanes, Eq. (33).[42]



(32)

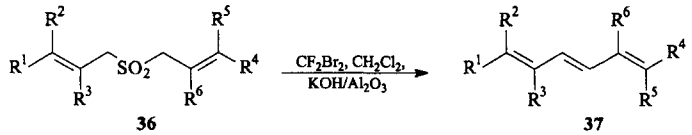
1. n = 0, oxone, MeOH; 2. n = 0, KOH-Al_2O_3, *t*-BuOH; 3. n = 0, $LiAlH_4$, THF; 4. SO_2Cl_2, CCl_4;

5. n = 1, NaOMe, MeOH, MeO_2C—C$_6$H$_4$—$CH_2S(C{=}S)OMe$ ... n = 0, 1, 2



(33)

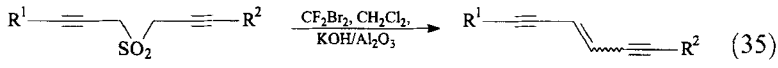
Starting from diallyl sulfone **36**[43] various conjugated 1,3,5-hexatrienes **37**, an important structural unit in a variety of natural products such as phytoene, vitamins D_2 and D_3, leukotrienes B_4 and C_4, asukamicin and mocimycin, have been prepared[43] by the above modified one-pot Ramberg–Bäcklund rearrangement, Eq. (34).[40] It is important to note that the stereoselectivity of this reaction is dependent upon the reaction conditions, and that it is possible to maintain a high level of stereocontrol in the formation of 1,3,5-trienes by appropriate choice of solvent and temperature. Thus, the (*Z*,*E*,*Z*)-triene isomer could be isolated in a 91 : 9 ratio in favor of the (*Z*,*Z*,*Z*)-isomer when the reaction was conducted at −78 °C in *t*-BuOH–CBr_2F_2 (1 : 1) solution, starting from the di-(*Z*)-cinnamyl sulfone **36**. However, when methanol was employed as the solvent, only the (1*E*,3*E*,5*E*)-triene was obtained, indicating a substantial loss of the stereointegrity of the terminal double bonds.



36 **37**

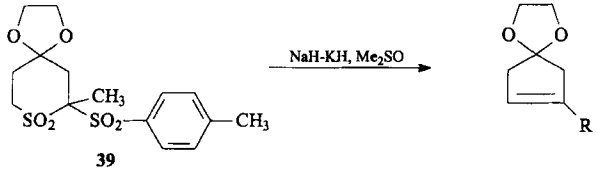
(34)

Chan's modification[40] of the Ramberg–Bäcklund rearrangement has also been used for the conversion of the dipropargyl sulfone **38** to the corresponding enediyne unit without the necessity to prepare an α-halo dipropargyl sulfone precursor in a separate step, Eq. (35).[44] It is noteworthy that the previously described protocol, CBr_2F_2, KOH/Al_2O_3, *t*-BuOH,[40] invariably led to intractable reaction mixtures, indicating the unsuitability of a protic solvent for these sulfone substrates. However, when CH_2Cl_2 was used in place of *t*-BuOH, the reaction proceeded smoothly at $-10\,^{\circ}C$ to give a readily separable mixture ($\sim 1:1$) of the (*E*)- and (*Z*)-enediynes.



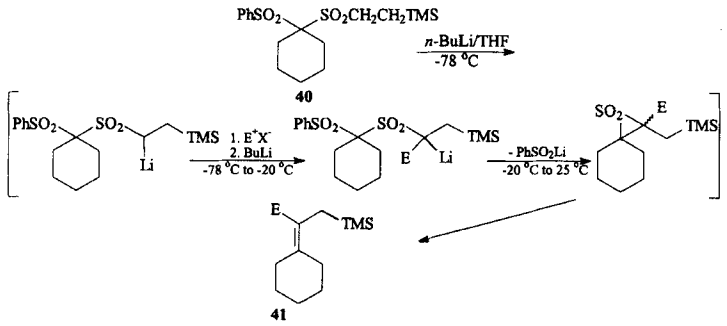
38 (35)

Matsuyama and coworkers[45] have found that *p*-toluenesulfinate ion acts as a good leaving group and may be used instead of a halogen anion under Ramberg–Bäcklund type reaction conditions. The alkylated (*p*-tolylsulfonyl)thiane dioxides **39** have been thus successfully converted in good yield to the corresponding cyclopentenes by the action of NaH-KH in Me_2SO, Eq. (36).

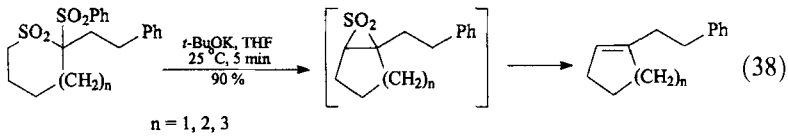


39 (36)

The same type of Ramberg–Bäcklund rearrangement[45] has been applied by Fuchs[46] for the conversion of the β-silylethyl α-sulfonyl sulfones **40** to the allylsilanes **41**, Eq. (37), and for the preparation of cycloalkenes, Eq. (38).[47]

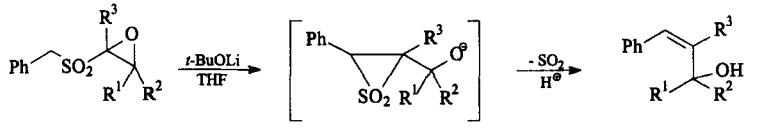


40 **41** (37)



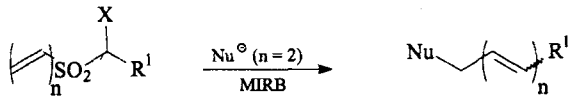
n = 1, 2, 3 (38)

One further variant of the Ramberg–Bäcklund rearrangement, namely, the epoxy Ramberg–Bäcklund rearrangement (EPRB), has been developed by Taylor.[48] In this reaction α,β-epoxy sulfones, on treatment with base, are converted into a range of mono-, di- and tri-substituted allylic alcohols. In this modification the leaving group is incorporated into a three-membered ring, Eq. (39). The key step involves a favored 3-*exo-tet* ring opening, but proceeds via a strained 1-hetera-4-thiaspiro[2.2]pentane transition state. A major advantage of this new reaction is that the alkene formation is accompanied by the introduction of additional functionality in the adjacent position. In terms of stereoselectivity, most systems gave a 1 : 1 *E*/*Z* mixture of products, but the stronger bases LHMDS and *t*-BuOK/LDA gave mainly the *E*-alkenes.

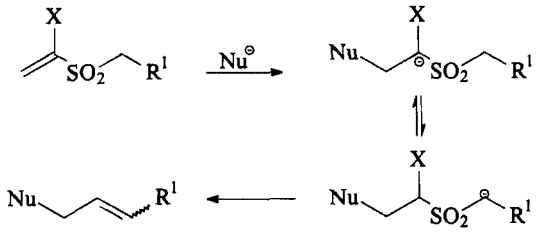


(39)

Taylor and Evans[49] suggested a further modification of the Ramberg–Bäcklund rearrangement, a new variant of the Michael induced Ramberg–Bäcklund rearrangement (MIRBR). MIRBR[50] circumvents the use of strong base for the formation of α-sulfonyl carbanions, involves addition of a suitable nucleophile to α-haloalkyl sulfones carrying a Michael acceptor system attached to the α'-position and allows introduction of functionality during the reaction, Eq. (40). In practice, however, the process is apparently limited to dienyl sulfone substrates and thus, leads to a diene synthesis. A novel version[49] of MIRBR allows producing allylic alcohols, sulfides and amines, Eq. (41).

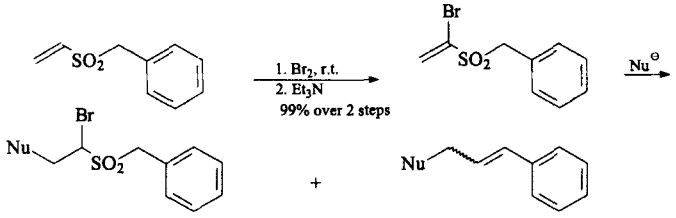


(40)



(41)

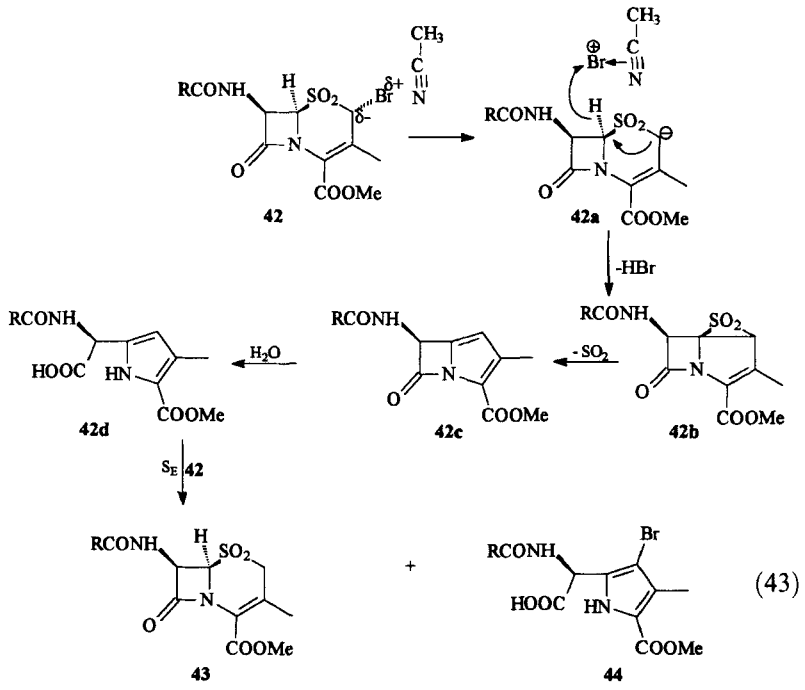
This new variant of MIRB has several interesting features, most notably the use of α-halovinyl sulfones as substrates. With an appropriate choice of substituents in the α-halo sulfones and of the reaction conditions, a one-pot tandem conjugated addition–proton exchange-RBR is possible, Eq. (42). The stereochemical output of this MIRBP is a mixture of E/Z-isomers and the $E:Z$ ratios reflect the basicity of the reagent.[48] With the weak amine bases, *cis*-isomers predominate, whereas methoxide and *t*-butoxide favor the formation of the *trans*-alkenes. In terms of mechanism of allylic amine forming reactions, there is the possibility that they proceed *via* intermediary sulfonyl aziridines, Eq. (39),[48] rather than as shown in Eq. (41).



(42)

Nu = MeONa, BnSH, $BnNH_2$, *t*-$BuNH_2$, (*S*)-$PhCHMeNH_2$, $MeCH(CO_2Me)_2$

A new type of Ramberg–Bäcklund rearrangement was recently described for the 2α-bromocephem sulfone **42**.[51] This sulfone on standing in acetonitrile solution results in roughly a 1 : 1 mixture of debrominated product **43** and the bromopyrrole **44**, Eq. (43).

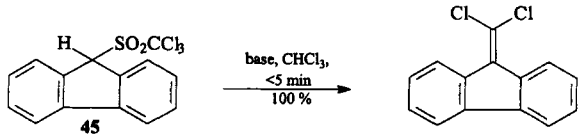


(43)

Since no basic conditions were involved in this reaction, these results were explained by the mechanism shown in Eq. (43). After SO_2 elimination the highly strained ring system **42c** splits very easily, yielding **42d** which, in turn, is brominated by **42** to the end product **44**.

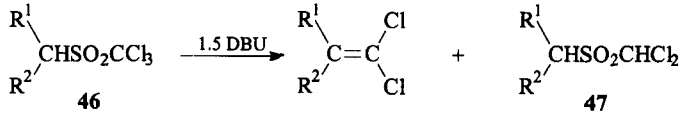
3.3. The Ramberg–Bäcklund Rearrangement of Trihalo Substituted Sulfones and Sulfoxides

Recently, Braverman and Zafrani reported an unusually facile Ramberg–Bäcklund rearrangement of α-trihalomethyl sulfones e.g. **45**.[52] This reaction proceeds spontaneously at room temperature on treatment with various weak bases, including DBU, Et_3N, Dabco, morpholine and even 2,6-lutidine, resulting in the formation of dichloromethylene products, Eq. (44).



(44)

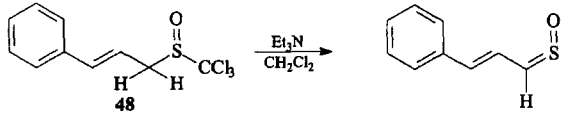
The benzyl trichloromethyl sulfones **46** rearrange under more drastic conditions and the corresponding dichloromethyl sulfones **47** are also formed as minor by-products, Eq. (45). Their formation may be explained by a simultaneous nucleophilic attack of the base on chlorine with subsequent protonation of the thus formed α-sulfonyl carbanion. The drastic conditions required for the Ramberg–Bäcklund rearrangement of benzylic sulfones have been attributed to the decreased acidity of their α-hydrogens as well as the reduced stability of the corresponding carbanions, relative to the fluorenyl sulfone **45**.



(45)

$R^1 = R^2 = p\text{-}ClC_6H_4$; $R^1 = R^2 = C_6H_5$; $R^1 = C_6H_5$, $R^2 = CH_3$

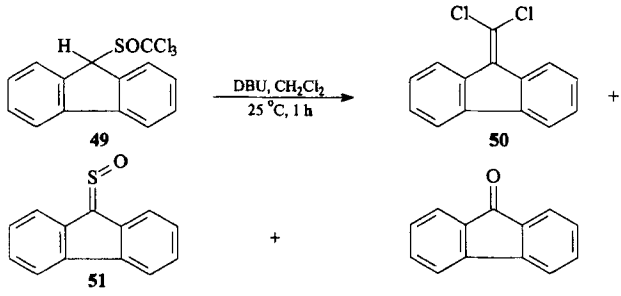
The Ramberg–Bäcklund rearrangement of these α-trichloromethyl sulfones is rather interesting in relation to the recently discovered β-elimination of chloroform from allyl and benzyl trichloromethyl sulfoxides, Eq. (46).[53] Since the first step, a fast reversible deprotonation of the starting material to give the corresponding carbanion, is common to both reactions, this widely different behavior of the trichloromethyl sulfones **45** and **46** and the trichloromethyl sulfoxides **48** represents a remarkable contrast of 1,3- vs. 1,2-elimination from the same carbanion center. This contrast is tentatively explained by the lack of stability of sulfenes in general.[54]



(46)

It is interesting to note that, unlike other trichloromethyl sulfoxides,[53] the 9-fluorenyl sulfoxide **49** is able to undergo both processes, the β-elimination of chloroform and the Ramberg–Bäcklund-type rearrangement simultaneously upon treatment with DBU in various aprotic solvents, yielding a mixture of the dichloromethylene product **50**, the 9-fluorenylsulfine **51**, and its oxidation product fluorenone, Eq. (47).[53b] Although the formation of **50** is dependent on the nature of solvent and base, it always appears as a by-product, except when

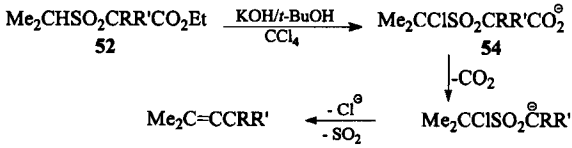
Et_3N is used in $CHCl_3$, where the Ramberg–Bäcklund product **50** is the only product.



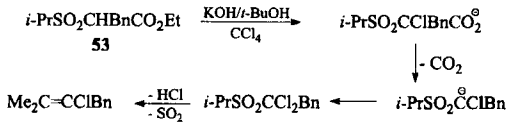
(47)

3.4. The Ramberg–Bäcklund Rearrangement of Sulfonyl Carboxylic Esters

Recently, Wladislaw[38a] and coworkers described the Ramberg–Bäcklund rearrangement of some α-isopropylsulfonyl carboxylic esters **52** and **53** in which the carbanion was generated by the decarboxylation of the ester, Eq. (48). In the case of the dialkyl substituted derivatives **52**, a chlorination at the isopropyl group should occur initially and then the intermediate **54**, due to the electron-withdrawing effect of the chloro substituted isopropyl group, would undergo decarboxylation to give a carbanion. The latter reacts by 1,3-displacement of chloride ion to give the corresponding episulfone precursor of the alkene. For the monoaryl derivatives, the resulting alkenes were in admixture with chloroalkenes, and in the case of the monobenzyl derivatives **53** the chloroalkene was the only reaction product. The formation of chloroalkenes may be explained by chlorination of the benzyl group instead of the isopropyl group. The resulting α-chloro carboxylate undergoes decarboxylative chlorination, followed by 1,3-elimination of chloride ion from the intermediate dichloro derivative, Eq. (49).



(48)

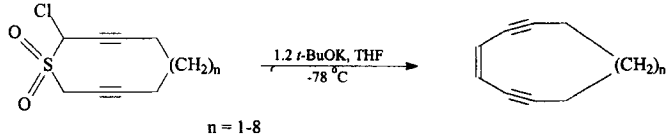


(49)

3.5. *Synthesis of Cycloalkenes* via *Ring Contraction*

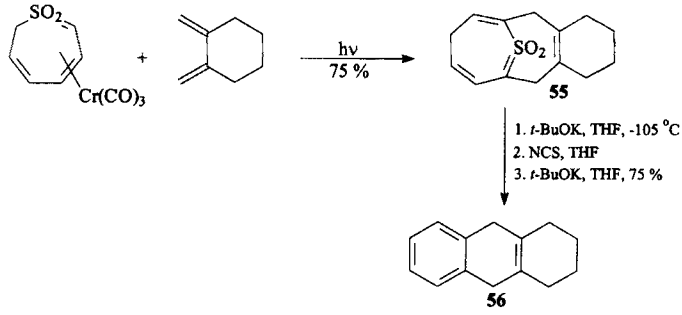
The Ramberg–Bäcklund rearrangement represents one of the first alkene syntheses in which the position of the double bond is clearly defined. One of the significant areas of application of the Ramberg–Bäcklund rearrangement is the preparation of various cycloalkenes by ring contraction. Some examples cited below demonstrate this strategy.

For example, Nicolaou and coworkers[55,56] have used the Ramberg–Bäcklund rearrangement for the preparation of a series of cyclic conjugated enediynes related to the natural anticancer antibiotics calicheamicin and esperamicin, Eq. (50).



(50)

This ring contraction approach was also used[57] in a novel benzannulation sequence based on a chromium(0)-promoted $[6\pi + 4\pi]$ cycloaddition, followed by a Ramberg–Bäcklund rearrangement, Eq. (51).

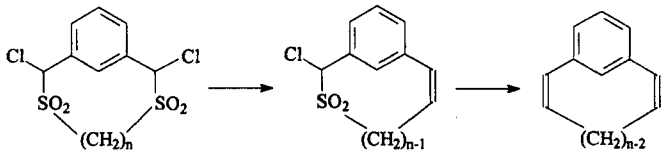


(51)

A noteworthy feature of this dual operation methodology was the simultaneous production of two rings during the cyclization.

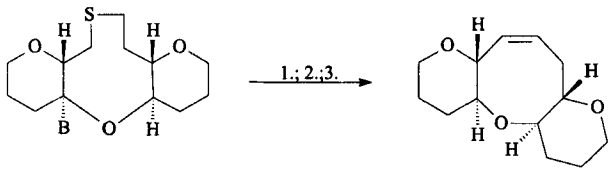
Treatment of the cycloadduct **55** in one pot with *t*-BuOK in THF at −105 °C, followed by trapping of the intermediate carbanion with NCS and exposure of the resultant mixture to a second equivalent of *t*-BuOK, afforded the hexahydroanthracene **56** in quite good yield. It has been shown that the efficiency of the ring contraction step is dramatically improved by employing *N*-iodosuccinimide instead of NCS as positive halogen source. Iodide is known to be a superior leaving group in this type of transformation.[24]

The same strategy has also been used[58] for the conversion of several 3,n-dithiabicyclo[n.3.1]-alkatrienes to the corresponding bicyclo[n.3.1]-alkapentaenes, Eq. (52). The chlorination of 3,n-dithiabicyclo[n.3.1]-alkatrienes has been examined carefully in terms of the significance of this step in the synthesis of bridged system *via* Ramberg–Bäcklund rearrangement. It has been shown that chlorination had occurred, as expected, at the benzylic position with highly purified NCS. Unlike the data of Paquette[59] and Tuleen,[60] i.e. that geminal dihalogenation is enhanced by the introduction of the first halogen atom, since the α-hydrogen becomes more acidic, the same product, the bis-(α-chloroalkyl) sulfide, was obtained by the use of two or four equivalents of NCS. This may reflect the crowded nature of this cyclic system.



(52)

Martin and coworkers have described a new technology for the construction of unsaturated medium-size tricyclo-[61] and bicyclo-polyether[62] frameworks, synthons for the total synthesis of ciguatoxine. Their synthetic strategy was based on thioannulation of *O*-linked oxacyclic precursors and successive α-halogenation and oxidation at sulfur, followed by a Ramberg–Bäcklund reaction, Eq. (53). One of the great strengths of this approach is that the position of the newly introduced double bond is fixed by the position of the sulfone group in the heterocycle and does not change under the reaction conditions.

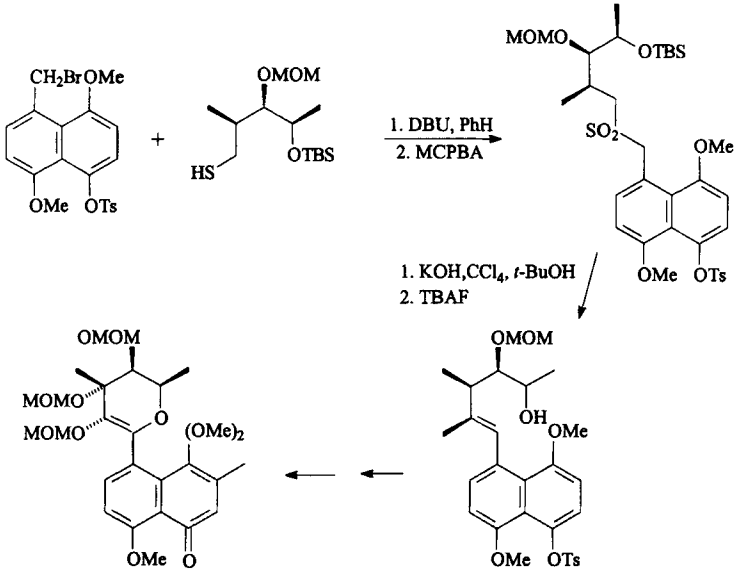


(53)

1. 1.5 equiv. NCS, CCl_4, 0 °C, 2 h; 2. 1.5 equiv. MCPBA, CH_2Cl_2, 0-25 °C, 3 h;
3. 1.2 equiv. *t*-BuOK, THF, 0 °C, 1.5 h, 52 %

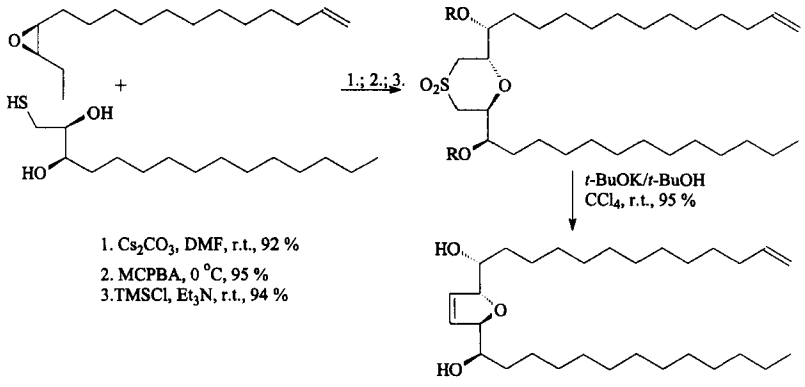
3.6. Convergent Approach in the Synthesis of Olefins

The Ramberg–Bäcklund rearrangement may be used for the coupling of two moieties via a sulfide linkage with subsequent oxidation and SO_2 extrusion resulting in the introduction of a double bond. This strategy was also applied to the synthesis of *C*-aryl glycosides[63] related to the antitumor antibiotic chrysomicine, Eq. (54).



(54)

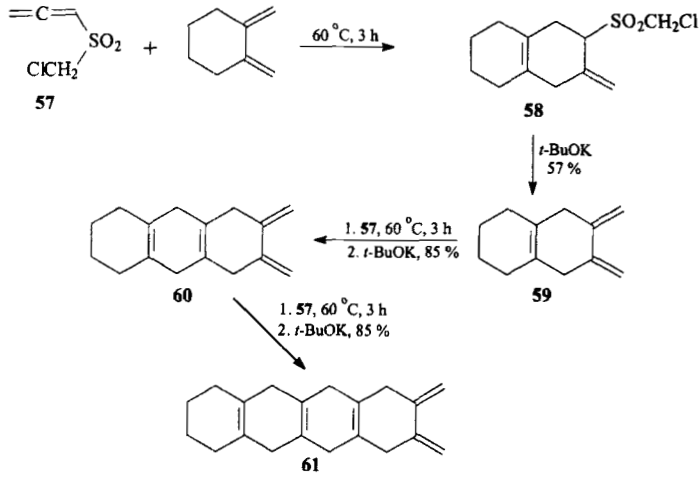
A general synthetic strategy[64] for the preparation of (+)-solamin and analogues, natural products with widespread activity from cytoxicity to antimalarial, immunosuppressant, and pesticidal, involved the same convergent approach in which two nearly equal halves were joined *via* a Ramberg–Bäcklund olefination, Eq. (55). The crucial step of the Ramberg–Bäcklund process was the chlorination because of possible failure to chlorinate either the sulfide or its corresponding sulfoxide. The best protocol involved *in situ* chlorination-rearrangement of the corresponding sulfone (the Meyers procedure).



(55)

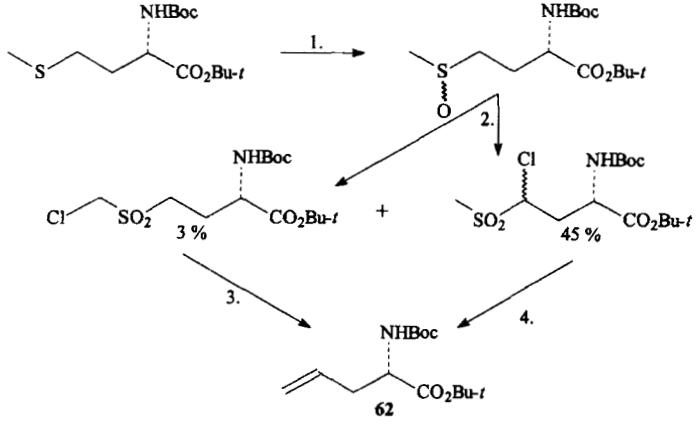
3.7. *Terminal Olefination*

Block[65] has successfully applied terminal olefination through Ramberg–Bäcklund rearrangement to a novel iterative ring growing procedure for the construction of linear fused carbocycles, Eq. (56). Allenyl chloromethyl sulfone **57** undergoes Diels–Alder cycloaddition with 1,2-bis(methylene)cyclohexane to give the intermediate **58** which under Ramberg–Bäcklund conditions (THF/*t*-BuOK) can be converted to a conjugated diene **59** ready for further reaction with sulfone **57**. Repetition of the process gave the tetraene **60** and then the pentaene **61**.



(56)

Another example of such terminal olefination was developed by Taylor[66] who explored sulfones derived from α-amino acids for the preparation of unsaturated α-amino acids in homochiral form. Equation (57) illustrates the conversion of methionine into allylglycine derivative. A low temperature was essential to minimize racemization. Optically pure **62** was obtained when the reaction mixture was kept below −30 °C.

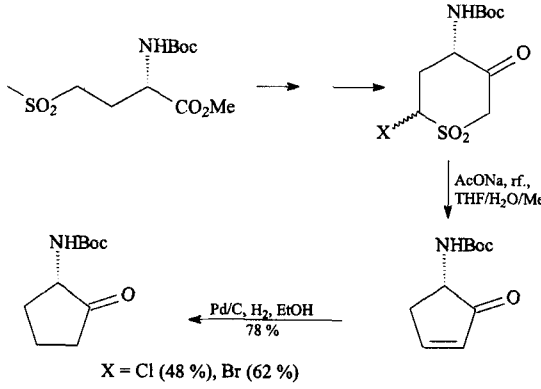


(57)

1. MCPBA, CH_2Cl_2, 94 %; 2. SO_2Cl_2, CaO, MCPBA, CH_2Cl_2; 3. *t*-BuOK, THF, -78 °C, 54 %; 4. *t*-BuOK, THF, -78 °C, 64-78 %.

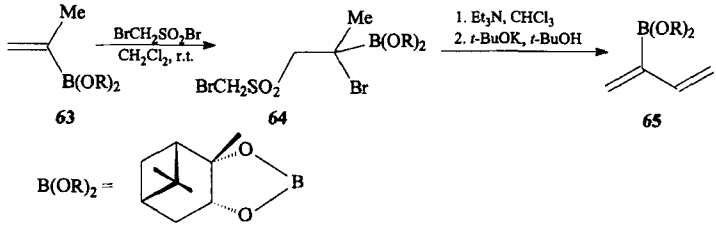
In related work[67] cyclic sulfones, derived from methionine and homocysteine, underwent the Ramberg–Bäcklund rearrangement and

gave substituted aminocyclopentenones, Eq. (58). Although racemization has occurred in this sequence, possibly during the Ramberg–Bäcklund step, it is possible to apply the Ramberg–Bäcklund approach to amino acid derived cyclic sulfones.



(58)

A useful application of the Ramberg–Bäcklund rearrangement involves direct the insertion of an α-halo sulfonyl group into an unsaturated starting material by means of free radical halosulfonylation.[68] Thus free radical addition of bromomethanesulfonyl bromide to the chiral vinyl boronate **63** gave the adduct **64** as a mixture of diastereomers which upon treatment with base afforded the diene **65** by a vinylogous Ramberg–Bäcklund rearrangement, Eq. (59).[69]

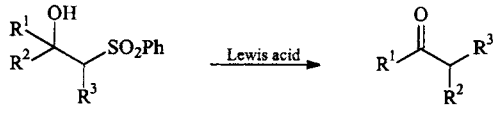


(59)

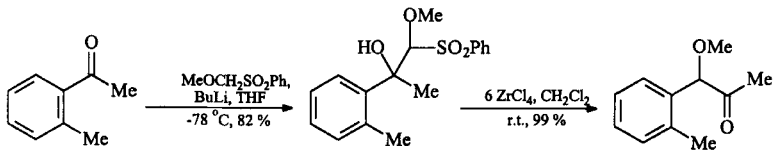
The utility of the Ramberg–Bäcklund rearrangement in the preparation of various natural products such as steroids,[70,71] nucleosides[72] or the naturally occurring furanone (+)-eremantholide A[73] has been demonstrated.

4. PINACOL REDUCTION OF β-HYDROXY SULFONES

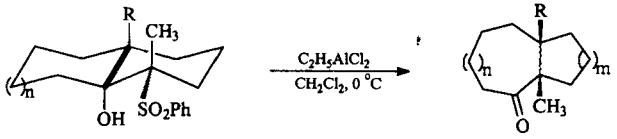
The Lewis acid catalyzed migration of an alkyl group from a β-carbon to an α-carbon with the concomitant elimination of a sulfonyl group leading to the formation of ketones has been observed with β-hydroxy sulfones, and has been termed as pinacol-reduction rearrangement Eq. (60). A variety of cyclic and acyclic β-hydroxy sulfones undergo the pinacol-reduction rearrangement, and this method has also been used for the homologation of ketones, Eq. (61).[74] The applicability of this rearrangement for a wide variety of substrates has been demonstrated. As shown by Trost and coworker,[75] this rearrangement is regioselective and requires a *trans* periplanar arrangement of the migrating bond and the sulfone leaving group. The conformationally rigid *trans* β-hydroxy sulfones **66** undergoes the pinacol-reduction type rearrangement in the presence of aluminum Lewis acids with very high regioselectivity, and yields bicyclic ketones **67**, Eq. (62).



(60)



(61)

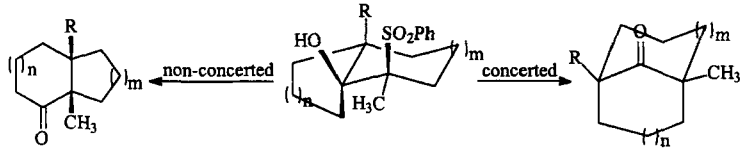


66a-d **67a-d**

(62)

a, R = H	m = 1	n = 1
b, R = H	1	2
c, R = H	2	1
d, R = CH_3	1	1

On the other hand, the conformationally less rigid *cis*-β-hydroxy sulfones **68** gave a mixture of bridged ketones **69** and fused bicyclic ketones **70**. The former product arises from the expected *trans* periplanar migration by a concerted reaction mechanism. The formation of the *cis*-fused bicycles **70** suggests that there is a non-concerted pathway in operation, Eq. (63).



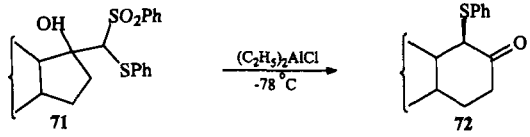
70a-d **68a-d** **69a-d**

a, R = H	m = 1	n = 1
b, R = H	1	2
c, R = H	1	3
d, R = CH_3	1	2

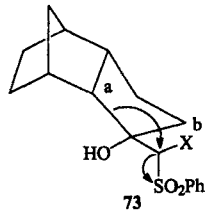
(63)

Lewis acids also influence the reaction mechanism, namely, the concerted *vs.* the non-concerted pathway. For instance, $Al(OSO_2CF_3)_3$[76] favors the formation of the bridged-ring **69d** as the major product (90%), arising from the non-concerted pathway for a *trans*-fused β-hydroxy sulfone.

Diethylaluminum chloride-mediated ring enlargement of the cyclic β-hydroxy α-phenylthio sulfones **71** to α-phenylthio ketones **72** has been studied by Trost and Mikhail, Eq. (64).[77]



71 **72**



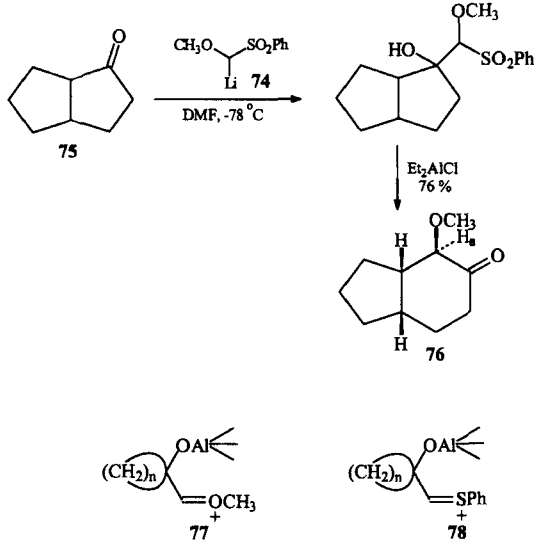
73

(64)

The migration of carbon takes place in such a way that the electron deficiency can be best stabilized in the transition state. An exception

could be due to the conformational rigidity of a five-membered ring of a norbornyl skeleton, as shown in **73**. Migration of bond 'a' proceeds through a boat-type transition state, whereas migration of bond 'b' proceeds through a half-chair conformation. Apparently, the migration of bond 'b' is the favored one and yields the observed product **72**.

The one-pot homologation of ketones to α-methoxy ketones has also be studied.[77] The addition of the lithium derivative of sulfone **74** to ketone **75** in DMF at −78 °C, followed by the addition of diethylaluminum chloride and work-up, gave the ring expanded product **76** directly, Eq. (65). In general, the observed regioisomer is formed *via* migration of the more substituted carbon. The abnormal behavior of ring expansion of bicyclo[2.2.1]heptyl systems has previously been noted.[78] As explained earlier in both cases, the conformational preference is for the chair rather than the boat form for the rearrangement. From the compounds **75** only one diastereomer is formed, probably the thermodynamically more stable isomer. The ring expansion of larger rings cannot be achieved with the lithium derivative of methoxymethyl phenyl sulfone **74**. The reason for this difference may be the better ability of oxygen *vs.* sulfur to stabilize the positive change. The higher stability of the presumed intermediate in the oxygen series, i.e., **76** compared with the sulfur series, i.e., **77**, may provide a smaller driving force for rearrangement.



(65)

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