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Ramberg-Bäcklund Rearrangement *vs.* β-Elimination of Haloform from Trichloro and Trifluoromethyl Sulfones

Samuel Braverman* and Yossi Zafrani

Department of Chemistry, Bar-Ilan University, Ramat-Gan 52900, Israel

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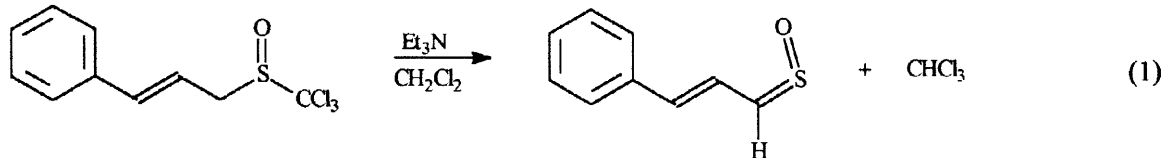
Abstract: A new and convenient method for the preparation of trichloro and trifluoromethanesulfinates is described. These esters readily undergo rearrangement to the corresponding sulfones at room temperature, in high yields. In contrast to trichloromethyl sulfoxides which undergo base-induced β-elimination of chloroform to sulfines, the corresponding sulfones undergo an unusually facile Ramberg-Bäcklund rearrangement with formation of dichloromethylene products. Replacement of CCl_3 by CF_3 results in complete loss of reactivity, even under drastic basic conditions.

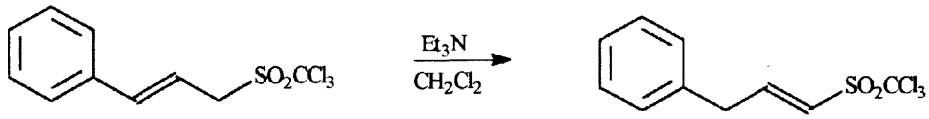
INTRODUCTION

Prompted by our recent discovery of a novel and highly efficient method for the synthesis of sulfines (thiocarbonyl S-oxides) via an unusual base-induced β-elimination of chloroform from allylic and benzylic trichloromethyl sulfoxides under mild conditions,[1] we became interested in the analogous synthesis of sulfenes (thiocarbonyl S,S-dioxides) from allylic trichloromethyl sulfones. However, allylic trichloromethyl sulfones are not suitable substrates for studying chloroform elimination due to their fast isomerization to vinylic sulfones under basic conditions. For example, while treatment overnight of cinnamyl trichloromethyl sulfoxide with



(1)

triethylamine in dichloromethane at room temperature results in β-elimination of chloroform and formation of thiocinnamaldehyde S-oxide (eq. 1), treatment of cinnamyl trichloromethyl sulfone under the same conditions results in complete and instantaneous isomerization to the corresponding vinyl sulfone (eq. 2)[2]. Consequently, we have turned our attention to the behavior of benzylic trichloromethyl sulfones under basic conditions.



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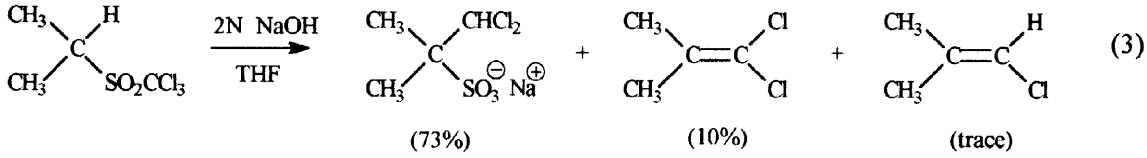
Interestingly, although the Ramberg-Bäcklund rearrangement of a wide variety of α-halosulfones has been thoroughly studied and extensively used as a once favored method for the synthesis of olefins,[3] the rearrangement of α-trihalomethyl sulfones has received only scarce attention in the literature. Furthermore, the drastic and aqueous alkaline conditions previously employed have led to mixtures of products and somewhat disappointing results. Thus, Paquette and Wittenbrook[4] have subjected several aliphatic trichloromethyl sulfones to reaction with excess 2N NaOH in refluxing aqueous THF in an attempt to elucidate the possible mechanistic pathways. The reaction was found to give rise to very small amounts of neutral products, except in those instances in which the dichloroepisulfone intermediate was gem-dialkyl substituted. Even then, sulfonic acid formation predominated, due to competing facile attack of the episulfone by hydroxide anions (eq. 3).

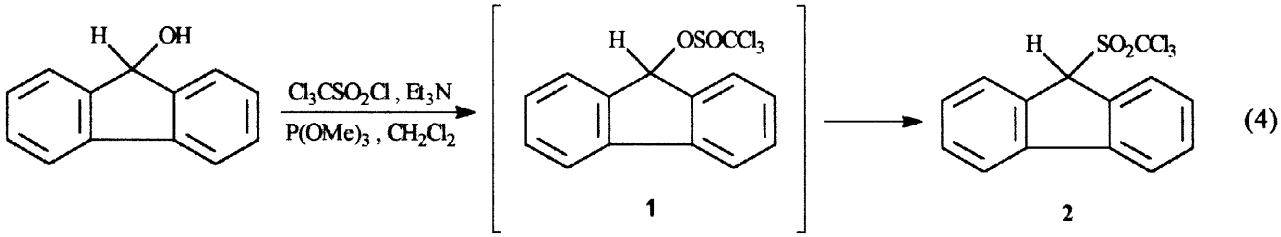


(3)

In this paper we wish to present our results on an unusually facile Ramberg-Bäcklund rearrangement under extremely mild and nonaqueous conditions. In addition, we report a new and convenient method for the preparation of trichloro- and trifluoromethyl sulfones which should prove of general interest in view of the well-known electron-withdrawing power of the trihalomethyl group.

RESULTS AND DISCUSSION

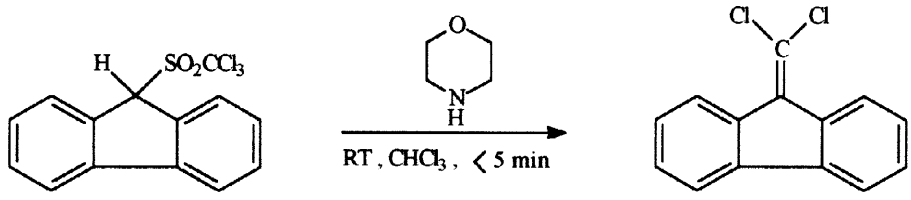
Trichloromethyl Sulfones. The required trichloromethyl sulfones are readily available by rearrangement of the corresponding trichloromethanesulfinates which in turn can be prepared by reaction of the appropriate alcohols with trichloromethanesulfinyl chloride, $Cl_3CS(O)Cl$. However, because of the high cost of the latter reagent, we prepared these sulfones by a modification of a procedure recently published by Klunder and Sharpless for the preparation of menthyl arenesulfinates.[5] This method, which is based on the reaction of alcohols with sulfinyl chlorides generated *in situ* by reduction of the corresponding sulfonyl chloride with trimethyl phosphite, is illustrated in equation 4 for the preparation of 9-fluorenyl trichloromethanesulfinate (**1**), which in turn undergoes spontaneous rearrangement to the corresponding sulfone in good yield (88%).



(4)

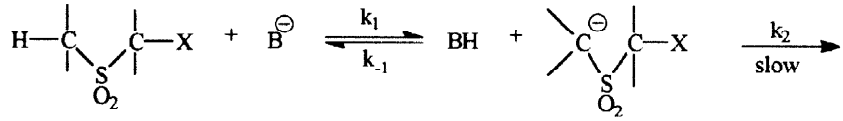
It may be interesting to note that our initial attempts to apply this method for the preparation of primary trichloromethanesulfinates under the exact conditions used by Sharpless to prepare menthyl trichloromethanesulfinate[5] resulted in complete failure. Only after lowering the temperature to -20°C, shortening the time to minimum, and reducing the amount of $(MeO)_3P$ to only one equivalent, was it possible to

use this method successfully, since the possibility of ester decomposition through nucleophilic displacement reactions by excess phosphite was avoided.[2] The same modified Sharpless procedure was used for the preparation of all trichloromethyl sulfones mentioned in this report. An alternative route involved preparation of the trichloromethanesulfenate ester by reaction of the appropriate alcohol with Cl_3CSCl, followed by either oxidation to the sulfinate derivative with MCPBA,[6] or followed by thermal rearrangement to trichloromethyl sulfoxides[7] and then oxidation of the latter with MCPBA.



2 3 (100%) (5)

Our investigation of β-elimination of chloroform from trichloromethyl sulfones was initiated with an examination of the behavior of 9-fluorenyl trichloromethyl sulfone. Surprisingly, we have found that instead of the expected β-elimination of $CHCl_3$ and accompanying sulfene formation, this compound (**2**) undergoes a spontaneous and apparently unprecedented Ramberg-Bäcklund rearrangement at room temperature, on treatment with various weak bases, and affords 9-dichloromethylenefluorene (**3**) in quantitative yield (eq. 5). The bases used include DBU, Et_3N, DABCO, morpholine and even 2,6-lutidine.



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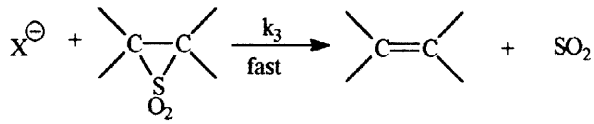
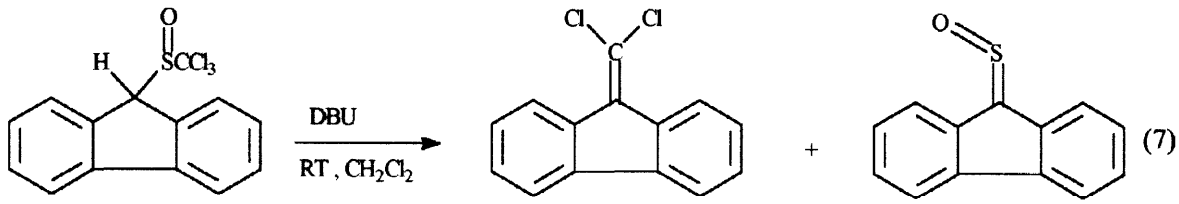


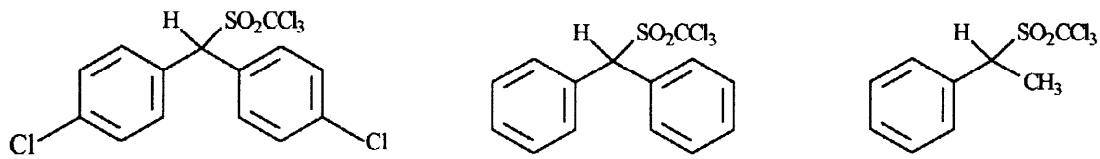
The Ramberg-Bäcklund rearrangement is one of the most important reactions of sulfones in general, and involves the conversion of α-halosulfones to olefins with accompanying loss of hydrogen halide and sulfur dioxide under basic conditions. The generally accepted mechanism shown in equation 6 is based on extensive mechanistic studies by Paquette and Bordwell.[8] These studies have shown that the reaction obeys second order kinetics, first order in each substrate and base and the mechanism suggested is of the reversible E1cB-type. In fact, the same type of mechanism could be expected for the β-elimination of chloroform as well. Furthermore, the first step, a fast reversible deprotonation of the starting material to give the stable 9-fluorenyl α-sulfonyl carbanion, is common to both reactions. The exclusive Ramberg-Bäcklund rearrangement in the case of trichloromethyl sulfone **2** on the one hand and the exclusive β-elimination of chloroform in the case of trichloromethyl sulfoxides on the other hand represent a remarkable contrast of 1,3- *vs.* 1,2-eliminations from

the same carbanion center. This contrast is tentatively explained by the lack of stability of sulfenes in general.[9] In this context, it is interesting to note that unlike other trichloromethyl sulfoxides, the 9-fluorenyl one (**4**) is capable of undergoing both processes simultaneously upon treatment with DBU in various aprotic solvents yielding a mixture of **3** and 9-fluorenylsulfine (**5**, eq. 7).[10] Although the formation of product **3** is dependent on the nature of the solvent and base, it always appears as a by-product, except when Et_3N is used in $CHCl_3$, where compound **3** appears as the only product.



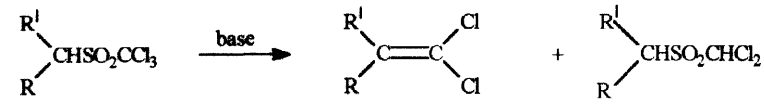
4 **3** (15%) **5** (85%)

In recent years, a number of modifications of the Ramberg-Bäcklund rearrangement have been reported with regard to both the structure of the sulfones employed and the reaction conditions. These modifications have opened new synthetic possibilities including the synthesis of natural products such as steroids, terpenoids and pheromones.[11] Recently, the rearrangement has also been applied to the synthesis of ene-diynes.[12]



6a **6b** **6c**

In order to improve the chances of β-elimination of chloroform and formation of the desired sulfene products, we have prepared the benzylic trichloromethyl sulfones **6a-c**, and tested their behavior under basic conditions. Since the acidity of the α-hydrogens of these compounds, as well as the stability of the correspondicarbanions is greatly reduced, a change in mechanism from E1cB to E_2 could be expected. In contrast to 9-fluorenyl trichloromethyl sulfone which undergoes spontaneous Ramberg-Bäcklund rearrangement, sulfones **6a-c** are relalively stable to all of the nitrogen bases mentioned above, except DBU. Even with this base, an excess amount of base is required, and besides the Ramberg-Bäcklund products **7a-c**, the appropriate dichloromethyl sulfones **8a-c** are also formed as minor by-products, thus indicating competing reduction of the sulfone at the α-position (eq. 8). This unexpected result may be tentatively explained by a simultaneous attack by the base on chlorine with subsequent protonation of the thus formed α-sulfonyl carbanion. However, the use of DMSO as solvent reduces the amount of the side product to minimum (e.g. 2% *vs.* 26% in $CHCl_3$, for sulfone **6b**).

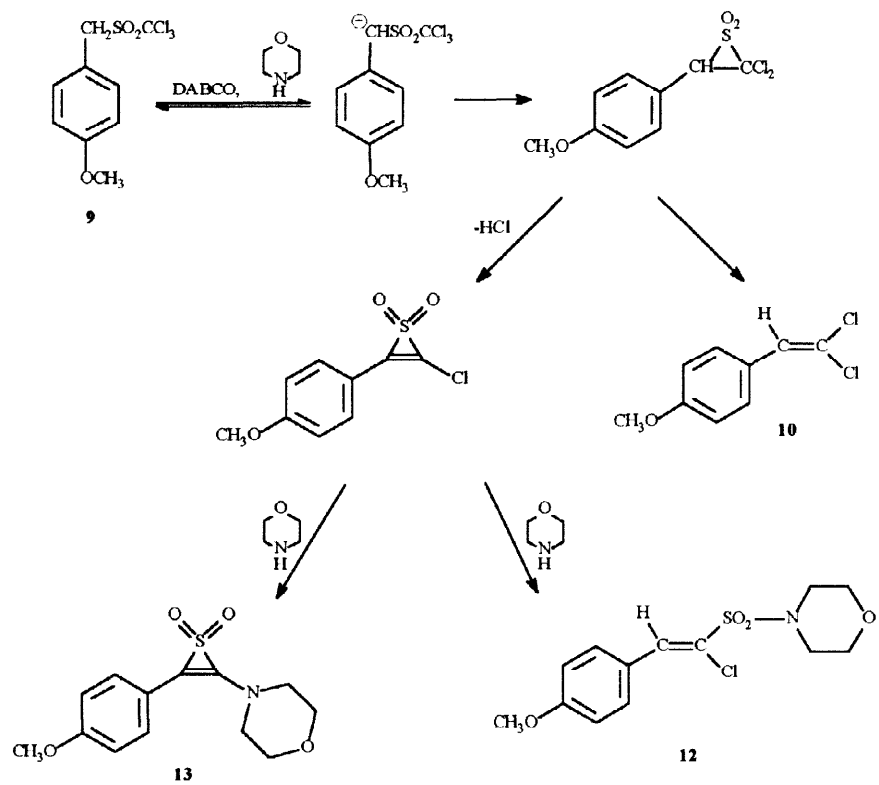


6a-c **7a-c** **8a-c** **(8)**

a, $R=R^1=p\text{-}ClC_6H_4$; **b**, $R=R^1=C_6H_5$; **c**, $R=CH_3$, $R^1=C_6H_5$

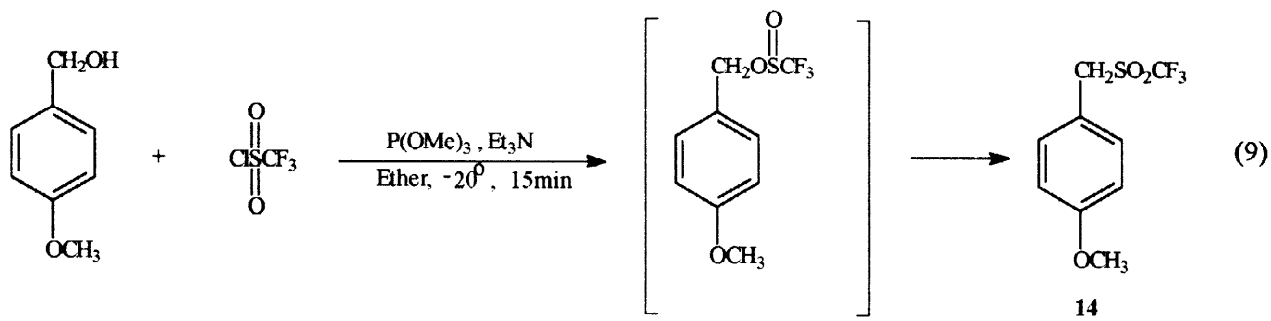
In view of these results and in order to further enhance the chances of chloroform elimination, we next performed the reactions of sulfones **6a-c** in refluxing toluene in the presence of DABCO and morpholine to trap any possibly generated sulfene. However, the Ramberg-Bäcklund rearrangement still occurred, and in quantitative yield, with no side products being formed. Consequently, and in order to further decrease the acidity of the α-hydrogens of the sulfone, *p*-anisyl trichloromethyl sulfone (**9**) was then examined. This compound was also prepared by the procedure described above from *p*-methoxybenzyl alcohol and Cl_3CSO_2Cl, and was obtained in high yield. We also expected the *p*-methoxy group to provide resonance stabilization of the desired sulfene product. The reaction of this compound in refluxing toluene for 1.5 hrs in the presence of DABCO and morpholine, resulted in the formation of the usual Ramberg-Bäcklund rearrangement product (**10**, 52% yield) as well as two minor products (**12**, **13**) arising by elimination of HCl from the episulfone intermediate and subsequent reaction of the thiirene dioxide with morpholine (Scheme 1). Finally, one should note that in spite of the unsuccesful attempts to detect β-elimination of chloroform, our discovery of an unusually facile preparation of dichloromethylene products is of considerable synthetic utility, including the synthesis of biologically active compounds.[13]

Scheme 1

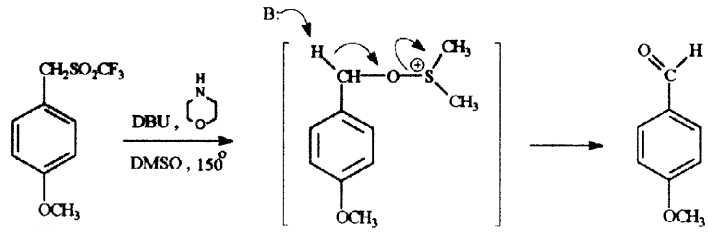


Trifluoromethyl Sulfones. The remarkable synthetic utility of the trifluoromethyl sulfones (triflones), established two decades ago by Hendrickson,[14] has been further demonstrated by Fuchs in recent years.[15] However, the cumbersome preparation of these sulfones tends to discourage their general use. One of the most efficient methods used so far is by thermal rearrangement of the corresponding trifluoromethanesulfinates (triflinates). The latter can be obtained by O-alkylation of the triflinate anion, when alkyl halides are treated with silver triflinate, or alternatively by reaction of alcohols with CF_3SOCl, which in turn must be prepared *in situ* by reaction of hygroscopic CF_3SO_2K with mesitylenesulfonyl chloride in acetonitrile.[14]

Due to the high cost and other problems involved with these methods, we examined the application of the method described above for the preparation of benzylic trichloromethanesulfinates to the preparation of triflinates. We were delighted to discover that these esters are also readily accessible by treatment of alcohols with commercially available CF_3SO_2Cl and trimethyl phosphite in the presence of Et_3N under mild conditions. In certain cases, such as *p*-anisyl triflinate, the ester undergoes spontaneous rearrangement to the corresponding triflone (**14**) in 80% yield (eq. 9).



Our success in developing a new and useful synthesis of triflones has enabled us to examine the effect of substitution of the CCl_3 by CF_3 group on the competition of 1,2- and 1,3-elimination. The drastically reduced chances of Ramberg-Bäcklund rearrangement in this case raised our expectations for fluoroform elimination and sulfene formation. However, all our attempts in this respect have met with failure. For example, treatment of *p*-anisyl triflone with 2 equivalents. of DBU in refluxing toluene for 24 hrs in the presence of morpholine acting as a trap, resulted in no change of the starting materials. Similar results have also been obtained with the benzhydryl triflone. Interestingly, however, using more drastic conditions such as heating of the *p*-anisyl triflone in DMSO at 150° for 4 hrs in the presence of 2 equivalents each of DBU and morpholine, afforded *p*-anisaldehyde. Formation of this unexpected product may be explained by direct or DBU mediated nucleophilic displacement of the triflinate group by DMSO, followed by elimination of Me_2S from the oxosulfonium intermediate (eq. 10). Although intramolecular displacement of the triflinate group and formation of cyclopropanes has already been observed by Hendrickson,[14] we are not aware of any intermolecular S_N2 displacement of the triflinate group, especially by weak nucleophiles such as DMSO or even DBU. In conclusion, although we succeeded in avoiding the Ramberg-Bäcklund rearrangement, we were still unable to

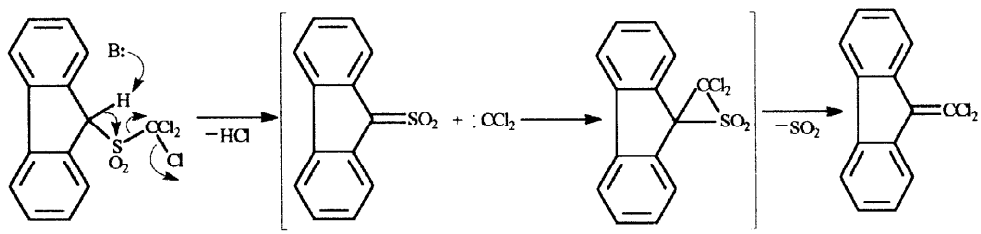


(10)

observe the desired β-elimination. We assume that the lack of stability of sulfenes in general and the high pK_a (31) of fluoroform[16] may be responsible for our results. Nevertheless, we believe that our discoveries of a new and efficient synthesis of triflinate esters, and a facile nucleophilic displacement of the triflinate anion from triflones, are of considerable synthetic and mechanistic significance.

Reaction Mechanism. In order to ascertain that the unusually facile Ramberg-Bäcklund rearrangement of the trichloromethyl sulfone proceeds by the generally accepted mechanism presented above (eq. 6), a brief kinetic study has been performed on the fluorenyl sulfone **2**. In view of the high reactivity of this compound, we first had to select an appropriate base of sufficiently low basicity whose ^1H NMR signals would not interfere with those of the starting material or product. *p*-Toluidine has thus been selected as the most suitable base for the kinetic study performed in various deuterated solvents. The rates of rearrangement were conveniently measured by the increase in intensity of the "ortho" protons' NMR signal at δ 8.3 of the product. The reaction of sulfone **2** showed second order kinetics, first order in each substrate and base. A plot of 1/a *vs.* t, using equal concentrations of both reactants, gave a straight line whose slope is k, the rate constant. Examination of the rate of hydrogen-deuterium exchange revealed that this reaction is much faster than the rate of rearrangement. This result indicates that the reaction proceeds by the reversible E1cB mechanism, as expected.

Consistent with this mechanism are also the effects of the polarity of the solvent and of the substituent on the reaction rates. Thus, the rate of reaction in CD_3CN ($k = 5.19 \times 10^{-4}$ $M^{-1}{}_{min}{}^{-1}$) is 315 times faster than in $CDCl_3$ ($k = 1.65 \times 10^{-6}$ $M^{-1}{}_{min}{}^{-1}$), while the reaction in DMSO-d_6 is completed within 5 min. at room temperature. This remarkable rate enhancement provides support of the E1cB mechanism, since the rate determining step of this mechanism is highly dependent on the carbanion concentration, which in turn is increased by the increase of the solvent ionizing power on going from $CDCl_3$ to CD_3CN. The importance of the stability of the carbanion intermediate is demonstrated by the observed reduction in rate in going from fluorenyl trichloromethyl sulfone (**2**) which reacts almost spontaneously even with weak bases such as 2,6-lutidine, to the benzylic sulfones **6a-c**, which undergo rearrangement only with strong organic bases such as DBU.



(11)

Finally, we should like to mention that in order to test the alternative mechanism shown in equation 11, we have also performed the reactions in the presence of suitable traps such as cyclohexene or morpholine for the expected dichlorocarbene and sulfene intermediates, respectively. However, no visible change in the reaction course could be detected, and no evidence for the alternative mechanism could be found, in spite of its mechanistic appeal.

EXPERIMENTAL

Melting points were obtained on a ThHoover melting point apparatus and are uncorrected. IR spectra were recorded on a Nicolet 60 SXB FTIR. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Brucker AC-200, Brucker DPX-300 or Brucker DMX-600 spectrometer in either $CDCl_3$ or other deuterated solvents and using TMS as internal standard. Chemical shifts are reported in δ ppm units, and coupling constants are in Hz units. High resolution mass spectra were obtained on a VG-Fison Autospec instrument. Mass spectra were obtained on a Finnigan GC/Ms 4021 instrument, by using either electronic ionization (EI) or chemical ionization (CI). Column chromatography was performed with Merck silica gel 60 (230-400 mesh), and TLC was performed on precoated Merck silica gel plates 60 F254. Dichloromethane was distilled from P_2O_5. Diethyl ether was dried over Na wires. Commercially available chemicals were used without further purification.

Trichloromethyl Sulfones, General Procedure. All the trichloromethyl sulfones have been obtained by rearrangement of the corresponding trichloromethanesulfinate esters. The latter were prepared by modification of the original Klunder and Sharpless procedure, as described below.

Equimolar quantities of the appropriate alcohol (1 mmole) and trichloromethanesulfonyl chloride, each dissolved in 10 mL of dry methylene chloride, were introduced into a 50 mL round bottomed flask, equipped with a magnetic stirrer and cooled to -20°C. To this solution, under a nitrogen atmosphere, were added gradually and simultaneously by means of a syringe equimolar quantities of triethylamine and trimethyl phosphite, After 15 min of further stirring at this temperature, the cooling bath was removed and stirring at room temperature was continued for various time intervals as indicated below for each product. The reaction mixture was then transferred to a separatory funnel, diluted with 100 mL of ether and washed 3 times with water, 3 times with 3% aqueous HCl, 3 times with 5% aqueous $NaHCO_3$, and again 3 times with water. After drying over anhydrous $MgSO_4$, filtration and evaporation of the ether, the desired product was usually obtained as a solid which was easily recrystallized from petroleum ether. Due to their high sensitivity to rearrangement to sulfones, all the compounds prepared except for the α-methyl benzyl ester were isolated as the corresponding trichloromethyl sulfones.

9-Fluorenyl Trichloromethyl Sulfone (2), was obtained by the general procedure in 88% yield after further stirring for half an hour at room temperature. M.p. 148° C. IR (neat): 1132, 1338 cm^{-1} (SO_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00 (d, J=7.5 Hz, 2H), 7.75 (d, J=7.14 Hz, 2H), 7.49 (t, J=8.2 Hz, 2H), 7.36 (t, J=6.75 Hz, 2H), 5.98 (s, 1H); ^{13}C NMR (200 MHz, $CDCl_3$): 141.7, 134.5, 130.2, 127.0, 120 (Ar), 69.7 (>CH); MS(EI):

m/e 350 (M^+, 3%), 348 (M^+, 9%), 346 (M^+, 10%), 165 (M^+-SO_2CCl_3, 100%). HRMS (Elemental composition): calc. ($C_{14}H_{10}O_2SCl_3$, MH^+) 346.946, obs., 346.950.

4,4'-Dichlorobenzhydryl Trichloromethyl Sulfone (6a) was obtained by the general procedure in 68% yield, after 12 hours of further stirring. M.p. 129-130° C. IR (neat): 1142, 1342 cm^{-1} (SO_2); ^1H NMR (200 MHz, $CDCl_3$), AA'XX' system: δ 7.64 (m, 4H), 7.4 (m, 4H), 6.15 (s, 1H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 136.0, 131.3, 130.4, 129.4 (Ar), 68.6 (>CH); MS(EI): m/e 416 (M^+, 7%), 235 (M^+ -SO_2CCl_3, 100%), 237 (64%), 239 (10%). HRMS (Elemental composition) calc. ($C_{14}H_9O_2SCl_5$, M^+), 415.876, obs., 415.904.

Benzhydryl Trichloromethyl Sulfone (6b) was obtained after 4 hours of further stirring, as a white solid, in 69%. M.p. 145-146° C. IR (neat): 1147, 1324 cm^{-1} (SO_2); ^1H NMR (200 MHz, $CDCl_3$): δ 7.73 (m, 4H), 7.4 (m, 6H), 6.21 (s, 1H); ^{13}C NMR (200 MHz, $CDCl_3$): δ 132.4, 130.2, 129.5, 129.0 (Ar), 70.3 (>CH). The compound decomposes during MS analysis.

α-Methylbenzyl Trichloromethyl Sulfone (6c) was obtained in 49% yield after the corresponding ester solution in $CHCl_3$ was heated under reflux for one hour. M.p. 60-61° C. IR (neat): 1150, 1341 cm^{-1} (SO_2); ^1H NMR δ (200 MHz, $CDCl_3$): δ 7.46 (m, 5H), 5.17 (q, J=7.1 Hz, 1H), 2.01 (d, J=7.1 Hz, 3H); ^{13}C NMR (200 MHz, $CDCl_3$): δ 133.5, 129.7, 129.6, 129.0 (Ar), 61.5 (-CH), 17.8 ($-CH_3$). MS (CI): m/e 304 (MNH_4^+, 100%), 308 (36%), 310 (3%), 270 (MNH_4^+-Cl, 17%). The compound was unstable to HRMS analysis.

***p*-Methoxybenzyl Trichloromethyl Sulfone (8)** was obtained in 85% yield by the use of the general procedure, except for the use of 1.25 equivalents of all reagents and further stirring for 15 min. at room temperature. M.p. 114-115° C. IR (neat) 1155, 1345 cm^{-1} (SO_2); ^1H NMR (300 MHz, $CDCl_3$): δ 7.4 (m, 2H), 6.95 (m, 2H), 4.74 (s, 2H), 3.83 (s, 3H); ^{13}C NMR (200 MHz, $CDCl_3$): δ 160.9, 132.8, 116.1, 114.7 (Ar), 55.3 (O-CH_3), 52.1 (CH_2); MS (CI): m/e 303 (MH^+, 12%), 305 (12%), 307 (4%), 121 (MH^+ - SO_2CCl_3, 100%); HRMS (Elemental composition) calc. ($C_9H_{10}O_3SCl_3$), 302, 942, obs., 302.982.

General Procedure for Ramberg-Bäcklund Rearrangement. To a solution of the appropriate trichloromethyl sulfone (1 mmole) in 10 mL of chloroform were added 1.5 eq of DBU. After 15 min of stirring at room temperature ether was added and the solution was washed consecutively 3 times with each water, 3% HCl, aqueous sodium bicarbonate and water again. The organic layer was dried over anhydrous $MgSO_4$, and the solvent removed under reduced pressure. All starting materials, except the 9-fluorenyl sulfone gave mixtures of both rearrangement and reduction products. Their data are listed below.

9-Dichloromethylenefluorene (4) was obtained as a yellow solid in practically quantitative yield within a few min. M.p. 120-122° C (lit m.p.=128-130°); IR (neat) 1647 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.3 (d, J=7.6 Hz, 2H), 7.69 (d, J=7.2 Hz, 2H), 7.38 (t, J=7.4 Hz, 2H), 7.3 (t, J=7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 140.1, 136.4, 129.0, 127.4, 125.7, 119.5 (Ar), 134.1 (Ar_2C=), 122.2 (=CCl_2); MS(EI): m/e 246 (M^+, 100%), 248 (75%), 250 (10%), 210 (M^+ - Cl, 8%), 176 (M^+ - 2Cl, 48%). All the spectral data are in good agreement with the published data.

2,2-*bis*-(4'-Chlorophenyl)-1,1-dichloroethene (7a) was obtained in 74% yield from the corresponding sulfone, as a viscous liquid. IR(neat) 1595 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.32 (m, 4H), 7.3 (m, 4H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 139.3, 137.4, 130.7, 128.6 (Ar), 134.3 (Ar_2C=), 120.6 (=CCl_2); MS(CI): 317 (MH^+, 66%), 319 (66%), 321 (100%), 281 (MH^+ - Cl, 98%), 283 (98.6%), 285 (43%), 246 (MH^+ - 2Cl, 70%), 248 (41%), 250 (9%). HRMS (Elemental composition) calc. ($C_{14}H_9Cl_4$) 316.9458, obs., 316.9540.

2,2-Diphenyl-1,1-dichloroethene (7b) was obtained in 63% yield from the reaction of the corresponding sulfone as a white solid. M.p. 62-65° C. IR(neat) 1600.9 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.3 (m, 10H); ^{13}C NMR (300 MHz, $CDCl_3$), δ 139.5, 129.2, 127.9, 127.2 (Ar); MS (CI): m/e 249 (MH^+, 24.5%), 251 (16%), 253 (2.8%), 213 (MH^+ - Cl, 42%), 215 (14%), 167 (MH^+ - CCl_2, 100%). HRMS (Elemental composition) calc. ($C_{14}H_{11}Cl_2$) 249.0237, obs., 249.0245.

2-Methyl-2-phenyl-1,1-dichloroethene (7c) was obtained in 73% yield from the reaction of the corresponding sulfone as a viscous oil. IR (neat) 1605 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.32 (m, 5H), 2.2 (s, 3H); ^{13}C NMR (200 MHz, $CDCl_3$): δ 140.1, 128.5, 127.5, 126.4 (Ar), 135.7 (>C=), 117 (=CCl_2), 23 (-CH_3); MS(CI): m/e 187 (MH^+, 55%), 189 (35%), 191 (5%), 151 (MH^+ - Cl, 100%), 153 (28%), 105 (MH^+ - CCl_2, 65.5%). HRMS (Elemental composition) calc. ($C_9H_8Cl_2$) 186.000, obs., 186.003.

4,4'-Dichlorobenzhydryl Dichloromethyl Sulfone (8a) was obtained in 26% yield as a viscous oil. ^1H NMR (200 MHz, $CDCl_3$): δ 7.57 (m, 4H), 7.4 (m, 4H), 5.92 (s, 1H), 5.89 (s, 1H); ^{13}C NMR (300 MHz, $CDCl_3$), 136.3, 131.3, 130.7, 129.7 (Ar), 77.6 ($CHCl_2$), 68.2 ($CHSO_2$); MS(CI): m/e 382.9 (MH^+, 8.7%), 384.9 (11.5%), 386.9 (6%), 388.9 (1.3%), 235 (MH^+ - SO_2CHCl_2, 100%), 237 (65%), 239 (14%). HRMS (Elemental composition), calc. ($C_{14}H_{11}SOCl_4$) 382.923, obs., 382.923.

Benzhydryl Dichloromethyl Sulfone (8b) was obtained in 37% yield as a white solid which was crystallized from hexane. As mentioned above, the formation of this as well as the following reduction products can be drastically reduced when a more polar solvent such asDMSO is used. M.p. 141-143° C. IR(neat) 1140.7, 1341.7 cm^{-1} (SO_2). ^1H NMR (300 MHz, $CDCl_3$): δ 7.66 (m, 4H), 7.43 (m, 6H), 5.93 (s, 1H), 5.91 (s, 1H); ^{13}C NMR (200 MHz, $CDCl_3$): δ 130.8, 130.1, 129.6, 129.3 (Ar), 77.6 (-$CHCl_2$), 69.7 ($CHSO_2$). The compound decomposes during MS analysis.

α-Methylbenzyl Dichloromethyl Sulfone (8c) was obtained in 27% yield as a yellowish oil. IR(neat) 1143, 1340 cm^{-1} (SO_2); ^1H NMR (200 MHz, $CDCl_3$): δ 7.45 (m, 5H), 5.8 (s, 1H), 4.83 (q, J=7.32 Hz, 1H), 1.88 (d, J=7.32 Hz, 3H); ^{13}C NMR (200 MHz, $CDCl_3$): δ 132.4, 129.8, 129.36, 129.33 (Ar), 76.6 ($CHCl_2$), 60.1 (CH), 14.4 (CH_3); MS(CI): m/e 270 ((MNH_4^+, 100%), 272 (69.5%), 274 (10%). The compound is unstable to HRMS analysis.

RB Rearrangement of *p*-Methoxybenzyl Trichloromethyl Sulfone (9). To a boiling toluene (2 mL) solution of DABCO (37 mg, 0.33 mmole) and morpholine (29 μL, 0.33. mmole), 50 mg (0.16 mmole) of the sulfone were added. After 12 hours of heating at the reflux temperature, 20 mL of ether were added, followed by

washings with water and drying over anhydrous $MgSO_4$. Removal of the solvent under reduced pressure afforded the following products which were separated by column chromatography.

2-*p*-Methoxyphenyl-1,1-dichloroethene (10) was obtained in 52% yield as a viscous oil. IR(neat) 1609 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 7.5 (m, 2H), 6.89 (m, 2H), 6.78 (s, 1H), 3.82 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 159.6, 128, 126 (Ar), 130 (>C=), 113 (=CCl_2), 55 (CH_3O-); MS(EI): m/e 202 (MH^+, 100%), 204 (63%), 206 (10%), 132 (M^+ - 2Cl, 7%); HRMS (Elemental composition) calc. ($C_9H_8OCl_2$) 201.9952, obs., 201.993.

***p*-Methoxybenzyl Dichloromethyl Sulfone (11)** was obtained in 5% yield as a white solid. M.p. 107-108° C. IR(neat) 1148.9, 1345.6 cm^{-1} (SO_2); ^1H NMR (200 MHz, $CDCl_3$): δ 7.39 (m, 2H), 6.95 (m, 2H), 6.03 (s, 1H), 4.54 (s, 2H), 3.83 (s, 3H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 160.8, 132.3, 116.9, 114.9 (AR) 77.1 ($CHCl_2$), 55.3 (CH_2), 53.9 (-OCH_3); MS(EI): m/e 267.9 (M^+, 29.3%), 269.9 (21.9%), 271.9 (6%), 121 (M^+-SO_2CCl_3, 100%); HRMS (Elemental composition) calc. ($C_9H_{10}O_3SCl_2$) 267.9727, obs., 267.975.

(Z)-1-Chloro-1-morpholinosulfonyl-2-*p*-methoxyphenylethene (12) was obtained in 4% yield as a yellow viscous oil. IR(neat): 1158, 1351, 1604 cm^{-1}; H NMR (200 MHz, $CDCl_3$): δ 7.62 (m, 2H), 6.94 (m, 2H), 6.78 (s, 1H), 3.87 (s, 3H), 3.78 (m, 4H), 3.35 (m, 4H); MS(CI): m/e 317 (MH^+, 39%), 319 (14%), 282 (MH^+ - Cl, 15.5%), 230.9 (MH^+-morpholine, 29%), 168.0 (MH^+-$SO_2N(CH_2CH_2)_2O$, 100%). HRMS (Elemental composition) calc. ($C_{13}H_{17}NO_4SCl$) 318.0566, obs., 318.052.

2-*p*-Methoxyphenyl-3-morpholinyl-thiirene-1,1-dioxide (13) was obtained in 6% yield as a yellowish viscous oil. ^1H NMR (200 MHz, $CDCl_3$): δ 7.54 (m, 2H), 6.92 (m, 2H), 3.86 (s, 3H), 3.85 (m, 4H), 3.24 (m, 4H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 134.7, 114.5 (Ar), 65.8, 46.3 (morpholine), 55.5 (OCH_3); MS(CI): m/e 282 (MH^+, 50%), 197 (MH^+ - morpholine, 11%), 218.1 (MH^+ - SO_2, 39%), 132 (MH^+ - SO_2 morpholine, 100%); HRMS (Elemental composition) calc. ($C_{13}H_{16}NO_4S$) 282.080, obs., 282.072.

4-Methoxybenzyl Trifluoromethyl Sulfone (14). To a cooled (-20° C) solution of *p*-methoxybenzyl alcohol (138 mg, 1 mmole) and trifluoromethanesulfonyl chloride (132 μL, 1.25 mmole) in 10 mL of dry ether, under a nitrogen atmosphere, were added simultaneously triethylamine (172 μL, 1.25 mmole) and trimethyl phosphate (147 μL, 1.25 mmole). After stirring for a further 15 min. the reaction mixture was brought to room temperature and washed 3 times each with water, 3% HCl, 5% aqueous $NaHCO_3$ and water. After drying over anhydrous $MgSO_4$ and removal of the solvent, the product was obtained as a white solid in 80% yield. M.p. 100-101°C (lit.[17] M.p. 100-101°C); ^1H NMR (200 MHz, $CDCl_3$): δ 7.34 (m, 2H), 6.95 (m, 2H), 4.43 (s, 2H), 3.83 (s, 3H); IR(neat): 1123, 1357 cm^{-1} (SO_2); MS(CI): m/e 272 (MNH_4^+, 19%), 138 (MNH_4^+ - CF_3SO_2, 27%), 121 (MH^+ - CF_3SO_2, 100%), 107 (MNH_4^+ - CF_3SO_2, - OCH_3, 31%).

Benzhydryl Trifluoromethyl Sulfone was prepared by the procedure described above for the preparation of the *p*-anisyl sulfone (**14**). M.p. 72-73° C; IR (neat) 1193, 1355 cm^{-1} (SO_2); ^1H NMR (300 MHz, $CDCl_3$): δ 7.66 (m, 4H), 7.36 (m, 6H), 5.62 (s, 1H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 130.0, 129.8, 129.5, 129.2 (Ar), 122.2, 117.9 (CF_3), 72.0 (CH). The compound is unstable for MS analysis

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