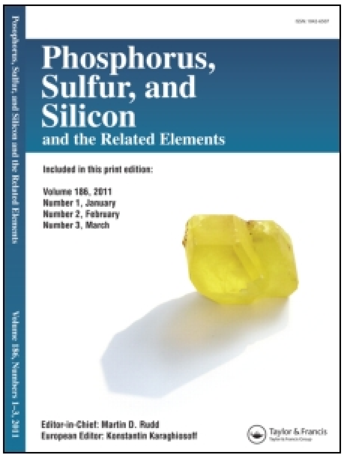

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# Methylenecyclopropanes in Elimination and Addition Reactions: Quantification of the Effects of Strain

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# Methylenecyclopropanes in Elimination and Addition Reactions: Quantification of the Effects of Strain

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*The effect of strain in 1,2-elimination reactions that form methylenecyclopropanes has been evaluated for a series of leaving groups. The worse the leaving group, the greater is the inhibitory effect of strain build-up, which reaches 50% of the excess enthalpy differential for the poorest leaving group studied.*

*In nucleophilic addition to an electrophilic methylenecyclopropane, comparison of strained and unstrained systems shows that about 60% of the excess enthalpy differential promotes the reactivity of the strained system.*

**Keywords** Addition; elimination; methylenecyclopropane; strain

## INTRODUCTION

The effect of strain on the rates of a range of reactions is qualitatively familiar.[2] Nucleophilic ring openings of epoxides, for example, occur readily under conditions in which unstrained ethers are inert.[3] We have previously quantified the effect of strain on elimination reactions.[4,5] In the systems chosen, the results showed that around 50% of the excess enthalpy difference[6] was expressed in acceleration of the reactions. Rate enhancements were of the order of $10^{11}$, but the results depended, because of the huge accelerations involved, on estimations of the reactivity of unstrained comparator systems. We now report on behavior in a system in which we can accurately quantify the reactivity of strained and unstrained systems under identical conditions. For eliminations in the strained systems on which we now report, the reactivity, instead of being increased, is inhibited by the accumulation of strain in the transition structure. As well as being able to quantify the effect of strain on an elimination reaction, we have been able to examine and measure

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Dedicated to Professor Marian Mikołajczyk, CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

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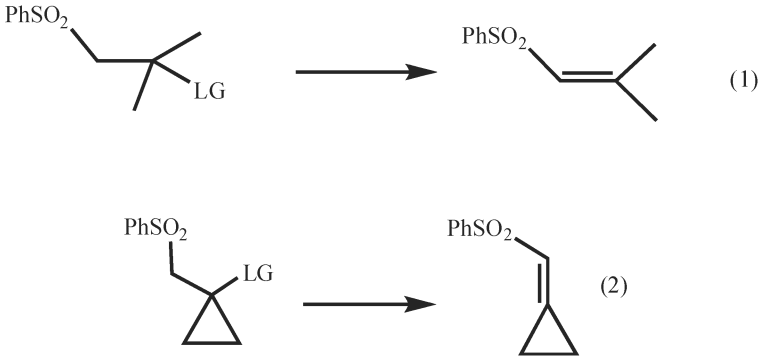
the effect of strain in the acceleration of nucleophilic addition to an electrophilic alkene.

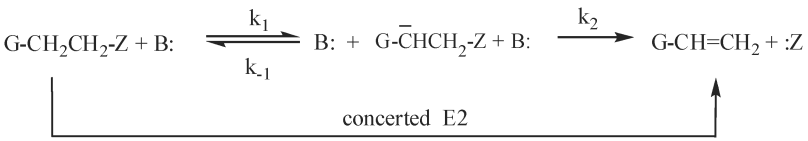
There are strict requirements to be met if meaningful conclusions are to be drawn from comparison of the reactivities of strained and unstrained systems. First, the comparison of strained and unstrained systems must be for reactions with the same unambiguous mechanism. Second, the strain energy differential must be accurately known, preferably from thermochemical measurements. Third, reactions must proceed in high yields, preferably to give a single product.

We have chosen to investigate the systems in Scheme 1. The behavior of sulfones in elimination reactions has been extensively studied in the past.[7,8] Sulfone carbon-acids have very high deprotonation/reprotonation rates,[9] so that in alkene-forming eliminations activated by sulfonyl groups, the very high deprotonation rates favor the $(\mathrm{E1cB})_R$ mechanism. In this mechanism, departure, $k_2$, of the $\beta$-leaving group becomes rate-determining as the pre-equilibrium $k_1/k_{-1}$ is rapidly established. This enables direct comparison both of ease of departure of leaving groups and attachment of nucleophiles[10] (Scheme 2).



**SCHEME 1**

Strain in methylenecyclopropanes has been discussed.[11] The strained angles of the cyclopropane ring—nominally 60 degrees—are even more strained in methylenecyclopropanes by the attachment of



**SCHEME 2**

the methylene group with $sp^2$ hybridization requiring a nominal C-C-C ring angle of 120 degrees. The resulting difference in strain between cyclopropane and methylenecyclopropane[12] is 54 $kJmol^{-1}$. In such systems, strain in the transition structure for an elimination reaction such as (2) in Scheme 1, presumably increases as the carbon–carbon double bond of the methylenecyclopropane is formed. Expression of strain differential will be reflected in the extent of double bond formation, and so the potential for inhibition of reactivity is considerable. The comparator system is reaction (1) in Scheme 1.

## METHODS AND RESULTS

### Substrates

In Scheme 3, the unstrained open chain halides **1** were obtained by homolytic addition of benzenesulfonyl halides to 2-methylpropene initiated by AIBN. Addition of thiophenol to the alkene **2** obtained by treatment of **1** with mild base gave the sulfide **3**. Subsequent oxidation gave the bis-sulfone **4**.

The strained systems were derived from methylenecyclopropane. The addition of halogens gave the dihalides **12**, and subsequent displacement with thiophenoxide gave the sulfides **13**. These, on oxidation, gave the sulfones **6**, which were also obtained by direct homolytic addition of sulfonyl halides to methylenecyclopropane.

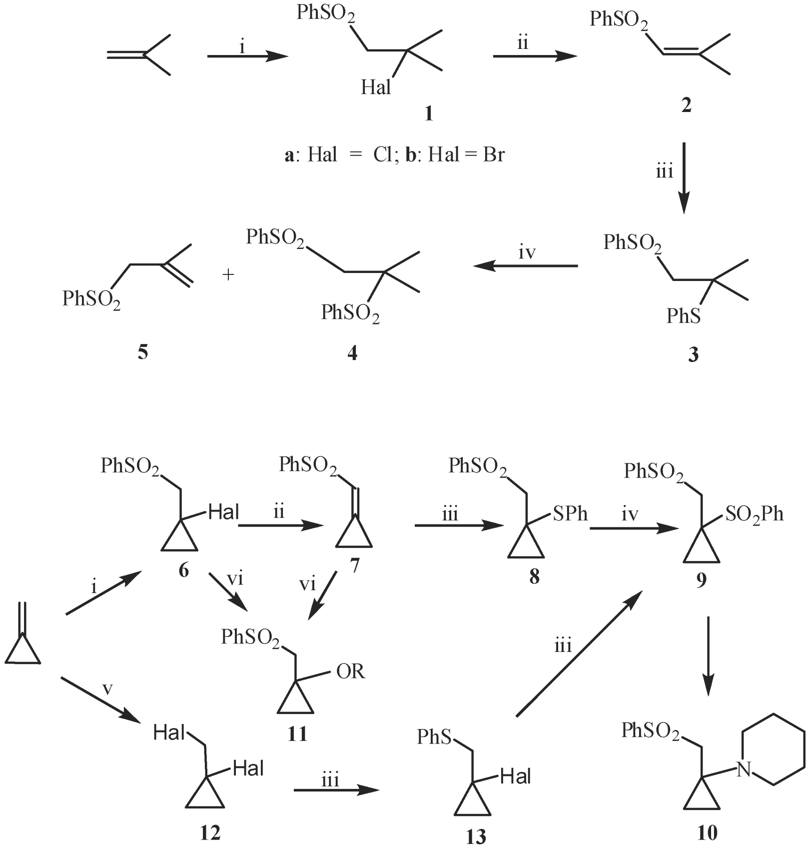
## DISCUSSION

### Eliminations

For the strained systems, formation of the alkene by activated 1,2-elimination increases the strain energy—excess enthalpy differential—by the difference in enthalpy between the starting material and the product. This differential amounts to 54 kJ $mol^{-1}$ and raises the question of the effect of the strain differential on the reactivity of the substrate. Data are in Table I. The expected products have been isolated in high yields, and the unstrained comparator substrates have been subjected to identical conditions.

#### *Pathways of the Reactions*

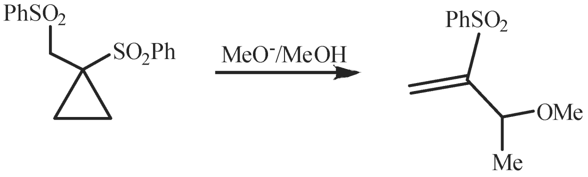
The possibility exists that for the sulfone leaving group, for example, the reaction with the base involves direct substitution rather than elimination–addition. The latter pathway has been shown to operate. Treatment of sulfone **9** with piperidine in ethanol gave no reaction,



i: $PhSO_2Hal$, AIBN, benzene, 90°, 72 h; ii: $Et_3N$-PhMe; iii: PhSNa-EtOH; iv: $H_2O_2$-AcOH; v: $Hal_2$-THF; vi: EtONa-EtOH; vii: EtONa-EtOH, piperidine.

**SCHEME 3**

but when sodium ethoxide was added, the product was the piperidinosulfone **10**. We conclude that piperidine is not sufficiently basic to cause elimination, but that when the methylenecyclopropane **7** is generated by the stronger base, ethoxide, **10** is formed, as piperidine is more nucleophilic than ethoxide ion. Earlier work[13] from another laboratory states that a different pathway is followed for the bis-sulfone **9**, which on treatment with methanolic sodium methoxide, gives the open-chain product **14** in low yield. In our work, we obtain high yields of the elimination-addition products **11**, R=OEt and **11**, R=OMe, and we have X-ray crystal structures for **9**, **11**, R=OEt and **11**, R=OMe. The properties of our specimen of **9** are quite different from those reported, but unfortunately a direct comparison has not been possible.[13]



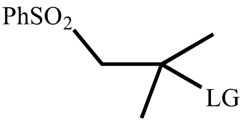
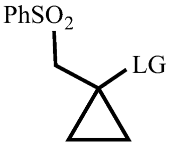
**9** **14**

The integrity of the cyclopropane ring under the reaction conditions was checked with sulfone **6**, Hal=H. There was no reaction.

## *Mechanisms of the Reactions*

Evaluation of the effect of strain requires that the rate-determining step of the reaction considered involves a process in which differential strain is felt. In the case of 1,2-eliminations activated by a $\beta$-sulfonyl group, earlier work has shown that, in an appropriate base-solvent system, for good leaving groups such as halogen, the reactions are either concerted ($E_2$) or ionization ($k_1$) that determines the rate.[10] For poor leaving groups, the pre-equilibrium is rapidly established. This allows the step, $k_2$, in which the leaving group departs, to be rate-determining. In the present systems, for the base-solvent system

**TABLE I Elimination to Form Unstrained and Strained Alkenes[1]**

| Rate constants/mol.$^{-1}$dm$^{3}$ s$^{-1}$ | | | | | |
|---|---|---|---|---|---|
| Leaving Group | Open Chain | | | Cyclopropane | |
| |  | | |  | |
| Z | | | $k_{rel}$ unstrained:strained | | |
| | $k_{obs}$[a,c] | $k_{ion}$[a,b,c] | | $k_{obs}$[a,c] | $k_{ion}$[a,b,c] |
| Br | $2.3\cdot10^{2}$ | $2.3\cdot10^{1}$ | **0.7** | $3.2\cdot10^{2}$ | $3.2\cdot10^{1}$ |
| Cl | $7.8\cdot10^{1}$ | $4.1\cdot10^{1}$ | **1.4** | $1.5\cdot10^{2}$ | $5.7\cdot10^{1}$ |
| $SO_2Ph$ | 3·44 | $8.8\cdot10^{2}$ | **229** | $1.5\cdot10^{-2}$ | $1.2\cdot10^{3}$ |
| SPh | $6.6\cdot10^{-2}$ | $4.8\cdot10^{-1}$ | **6168** | $1.0\cdot10^{-5}$ | $6.7\cdot10^{-1}$ |
| OMe | $4.3\cdot10^{-5}$ | 3·1 | **28666** | $1.5\cdot10^{-9}$ | $5.3\cdot10^{-1}$ |

[a] Units: $m^{-1}dm^{3}s^{-1}$; [b] See text; [c] For reactions in EtONa–EtOH at 25°C.

sodium ethoxide-ethanol, we have examined all of the reactions by $^2$H NMR for the incorporation of deuterium in the starting material from deuteriated solvent. Another criterion we have used for the diagnosis of the mechanism is to interpolate the ionization rate of the series of methylenecyclopropanes. In earlier work,[14] ionisation rates were determined for a series of $\beta$-substituted aryl ethyl sulfones. This information can be applied in the present systems to the difficult distinction between the $E_2$ and $(E1cB)_I$ mechanisms. In Table I, the interpolated ionization rate constants derived from a Taft plot[14] of $k_{ionisation}$ versus the inductive constant $\sigma^*$, can be compared with the overall elimination rate constants. When the leaving group is bromide, for both the strained and unstrained systems, the elimination rates are substantially greater than the ionization rates, $k_1$, pointing to a concerted mechanism, $E_2$. For chloride as leaving group, in both systems, the ionization rates are comparable with the elimination rates, suggesting, albeit not proving, that the $(E1cB)_I$ mechanism operates. In all of the other substrates, interpolated ionization rates are much larger than the elimination rates, consistent with operation of the $(E1cB)_R$ mechanism in which departure of the leaving group is rate-determining. This conclusion is strengthened by the observation of deuterium incorporation in the same substrates under the conditions of the elimination reactions.

Reactions were followed by UV spectroscopy for reactions in which the product alkene was detectable and otherwise by gc. All reactions were first order in substrate and first order in base. Results are in Table I. The expected products were formed in high yields (Table II).

## Evaluation of the Effect of Strain

Against this mechanistic background, the question of the involvement of strain can be considered. For the halogen leaving groups, the eliminations have either the $E_2$ or $(E1cB)_I$ mechanisms for both strained and unstrained substrates. Deprotonation is either coupled

**TABLE II Product Analysis for Elimination Reactions**

| Sulfone | LG | Product | Yield %[a] | Deuterium incorporation |
|---|---|---|---|---|
| **6a** | Cl | 11 | 90 | no |
| **6b** | Br | 11 | 81 | no |
| **8** | SPh | 11 | 90 | yes |
| **9** | $SO_2Ph$ | 11 | 95 | yes |
| **11**; R=Me | OMe | 11; R=OMe + R=OEt | 95 | yes |

[a] Of 1-Ethoxy-1-phenylsulfonylmethylcyclopropane **11**, R=OEt.

with loss of the leaving group or is itself rate-determining. There can be no evaluation of the effect of strain on these processes. For the other leaving groups, formation of the strained alkene is rate-determining, and the effect of strain can be commented on. The first striking feature of the results of Table I is that the reactivity ratio for the unstrained to strained substrates changes greatly as the leaving group is changed. In our work on nucleofugalities,[7] we established ranks (nucleofugalities) in $\beta$-eliminations from sulfones for a large number of leaving groups and determined the order $PhSO_2 > PhS \gg OMe$. In reactions with halides, as in the present cases, the mechanisms followed did not involve rate-determining loss of the leaving group. In the present systems, the reactivity ratio for the unstrained to strained substrates increases greatly as the leaving group is changed from phenylsulfonyl through phenylthio to methoxy. It can reasonably be inferred that as leaving group ability declines, as in this series, a greater double bond order in the transition structure is required to expel the leaving group. The associated energetic cost in this system is the involvement of an increasing proportion of the excess enthalpy of the product methylenecyclopropane.

The important associated question relates to the extent of the expression of the strain differential between the cyclopropane starting material and the methylenecyclopropane product. The most marked inhibition is seen in the case of the poorest leaving group, methoxy. In this case, a factor of 29000 between the strained and unstrained substrates corresponds to transition structure energy difference of about 26 kJ $mol^{-1}$ or about 50% of the strain energy differential. This statement is made on the assumption that the A factors for the two reactions are the same. Intriguingly, there is a large difference between the inhibitions observed with the sulfonyl and phenylthio leaving groups. The *nucleofugalities* of these groups are quite similar, and so the large difference in strain inhibition is not readily accounted for.

In an electrophilic addition to a methylenecyclopropane such as that of bromine, there appears to be a trade-off between the additional strain induced in the intermediate (spiro) bromonium ion and the increased stability afforded by attachment of the cyclopropyl ring to the intermediate cation.[15] The rate ratio for the addition of bromine to 2-methylpropene versus methylenecyclopropane is $10^2$, corresponding to a $\Delta E$ of 11.7 kJ $mol^{-1}$ against a strain energy difference of 27.2 $kJmol^{-1}$ or substantially less than 50%.

Within this context of the reactivity of cyclopropyl derivatives, 4-phenylsulphonylmethylcyclopropane (**6**, Hal = H) was inert to the conditions that caused elimination in the substrates in which there was a substituent in the ring as in **6**, **8**, **9**, and **11**.

## Nucleophilic Addition to Electrophilic Alkenes

Nucleophilic addition to alkenyl sulfones has been extensively investigated[16,17] quantitatively. Reactivity is extremely sensitive to substituents on the carbon–carbon double bond. Thus, attachment of a $\beta$-methyl group reduces reactivity in addition of piperidine in ethanol by a factor of 800 and for the $\beta,\beta$-dimethyl member of the series, tautomerization to the nonconjugated isomer **5** occurs faster than addition.[16] In the present work, we have investigated the effect of the release of strain as the hybridization of the carbon atoms of the double bond changes from $sp^2$ to $sp^3$.

The obvious comparison to make is between the strained alkene **7** and the open-chain analogue **2**, acknowledging that the there is a small steric difference between the two substrates. The methyl groups of the open-chain alkene possibly obstruct approach of the nucleophilic ethoxide ion somewhat more than the methylene groups of the methylenecyclopropane. On the other hand, the methylene groups of the methylenecyclopropane, in contrast to the methyl groups of the unstrained alkene, are not free to rotate. Comparisons are further complicated by the fact that direct addition to the open-chain analogue has not been observed; with piperidine as nucleophile, isomerization to the non-conjugated isomer is the result. In the light of these considerations, we decided to compare the reactivities of sulfones **2**, **7**, and phenyl vinyl sulfone **15** towards ethanolic sodium ethoxide. In the cases of sulfones **7** and **15**, the products were those expected from simple addition, namely **11** and 2-ethoxyethyl phenyl sulfone **16**[18] obtained in high yields. By contrast, sulfone **2** on treatment under the same conditions gave no addition product, but instead an equilibrium mixture of sulfones **2** and **5** in a ratio consistent with earlier work from another laboratory.[19] The rate of equilibration was measured by the loss of the UV absorption at 230 nm. Results are in Table III.

As seen above, for a powerful nucleophile such as piperidine, ß-methyl substitution in phenyl vinyl sulfone lowers reactivity. If it is

**TABLE III Rate Constants for the Reaction of Sodium Ethoxide with Vinyl Sulfones**

| Sulfone | $k_{obs}$. ($M^{-1}s^{-1}$) | Reaction |
|---|---|---|
| **15** | $3.38 \cdot 10^{-1}$ | Addition |
| **7** | $1.71 \cdot 10^{-1}$ | Addition |
| **2** | $3.78 \cdot 10^{-3}$ | Rearrangement |

assumed, even for the poorer nucleophile, ethoxide, that ß-methyl substitution has the same inhibitory effect and that a second ß-methyl group causes a further 800-fold diminution in the rate of addition, then the derived rate constant for the ß, ß-dimethyl sulfone **2** is $4.8 \cdot 10.^{-7}$ On this basis, the methylenecyclopropylsulfone **7** reacts faster by a factor of $3.5 \cdot 10.^{5}$ Converted into an energy of activation difference (assuming as before that A factors are the same), this amounts to 32 $\text{kJmol}^{-1}$ or about 60% of the energy difference between the strained and unstrained substrates.

## EXPERIMENTAL

### General

Solids were recrystallized to constant mp. Melting points were obtained on a Köffler hot stage and are uncorrected. Ethanol was dried by the magnesium iodine method. Extracts were dried over sodium sulfate.

### 2-Bromo-2-methyl-1-phenylsulfonylpropane 1b

Benzenesulfonyl bromide (3.47 g, 15.7 mmol) and AIBN (411 mg, 2.5 mmol.) were added to isobutene (1.1 g, 19.6 mmol) in benzene (5 mL). The mixture was kept at 63–65°C (sealed tube) for 72 h. Concentration of the solution gave an oil which on extraction with light petrol (5 × 20 mL) gave the sulfone (3.05 g, 70%) mp 56–57°C. $^1$H NMR ($CDCl_3$) $\delta$ 7.95 (d 2H, $J = 8.5$ Hz); 7.70–7.50 (m, 3 H); 3.80 (s, 2H), 2.15 (s 6H). IR $\text{cm}^{-1}$ 1321,1152 (s). MS, $M^+$ 279. Found: C, 43.4; H, 4.8; Br, 28.8; S, 11.3. $C_{10}H_{13}BrO_2S$ requires C, 43.3; H, 4.7; Br, 28.8; S, 11.6%.

Reaction of 2-bromo-2-methyl-1-phenylsulfonylpropane, **1b**, with ethanolic sodium ethoxide. The base solution (0.114 M, 2 mmol) was added to the sulfone (500 mg, 1.3 mmol) in ethanol (20 mL), and after 30 min, part (14 mL) of the mixture was quenched with saturated aqueous ammonium chloride (5 mL) and extracted with dichloromethane. Evaporation gave a mixture of alkenes (123 mg, 95%), which was by $^1$H NMR ($CDCl_3$) $\delta$ 7.85–7.80 (m, 2Ha+2Hb), 7.50–7.45 (m, 2Ha + 2Hb), 6.20 (s, 1Ha), 5.05 (s, 1Hb), 3.25 (s, 2Ha), 2.15 (s, 3Ha), 1.90 (s, 3Ha + 3Hb) a 10.5:1 mixture of the $\alpha,\beta$- and $\beta,\gamma$-alkenes **2** and **5**[19]. After 3h, the alkene ratio was 1.36:1.

### 2-Chloro-2-methyl-1-phenylsulfonylpropane 1a

Benzenesulfonyl choride (2.77 g, 15.7 mmol) and AIBN (411 mg, 2.5 mmol) were added to isobutene (1.1 g, 19.6 mmol) in benzene (5 mL).

The mixture was kept at 63–65°C (sealed tube) for 72 h when evaporation gave a brown oil, which on flash chromatography yielded the sulfone (920 mg), mp 51.5–52°C. (Lit.[20] 44–45°C). Reaction with ethanolic sodium ethoxide was as for **1b** and gave the alkene mixture in 96% yield.

## 2-Methyl-1-phenylsulfonylpropene 2

2-Bromo-2-methylpropyl phenyl sulfone **1b** (0.83 g, 39 mmol) in toluene (5 mL) was treated with triethylamine (4.5 mL, 39 mmol) in toluene (5 mL), and the mixture was boiled under reflux for 5 h. The addition of water (25 mL) and extraction with dichloromethane and evaporation of the extracts gave a residue, which on treatment with light petrol gave the alkene (570 mg, 74%), mp 50–51°C (lit.[21] 50°C).

## 2-Methyl-1-phenylsulfonyl-2-phenylthiomethylpropane 3

Alkene **2** (1.42 g, 7.2 mmol) was added to thiophenol (1.53 mL, 4.4 mmol) in ethanolic sodium ethoxide (5 mL, 7.2 mmol), and the mixture was refluxed for 6 h. The mixture was diluted with water (50 mL) and extracted with dichloromethane. The extracts were washed successively with aqueous 5% sodium hydroxide and water, and evaporation gave a brown oil (2.22 g). Flash chromatography (50:50 ethyl acetate:petrol) gave the sulfide (69%), mp 66°C (Lit.,[22] 65°C) $^1$H NMR ($CDCl_3$)$\delta$ 7.90 (d, 2H, $J=$ 8.5Hz), 7.71–7.30 (m, 8H), 3.35 (s, 2H), 1.60 (s, 6H); IR 1318, 1151(s); MS M+ 306. Found: C, 62.7; H, 6.0; S, 21.0. Required for $C_{16}H_{18}O_2S_2$: C, 62.7; H, 5.9; S, 20.9%. Reaction of the sulfide with ethanolic sodium ethoxide was as before to give the mixture of alkenes (98%).

## 1,2-Bis-phenylsulfonyl-2-methylpropane 4

Sulfide **3** (1.71 g, 5.6 mmol) was kept at 60°C in acetic acid (15 mL) while 30% hydrogen peroxide (14 mL, 120 mmol) was added dropwise. After 4h, the mixture was diluted with cold brine and extracted with dichloromethane. The extracts were washed with saturated aqueous sodium hydrogen carbonate and water. Evaporation gave the sulfone (58%), mp 159–160°C. $^1$H NMR ($CDCl_3$)$\delta$ 7.90–7.85 (m, 4H), 7.75–7.55 (m, 6H), 3.55 (s, 2H), 1.65 (s, 6H). IR 1305, 1152 cm$^{-1}$ (s). Found: C, 56.8; H, 5.3; S, 19.2. $C_{16}H_{18}O_4S_2$ requires C, 56.8; H, 5.4; S, 19.0%. Reaction of the sulfone with ethanolic sodium ethoxide was as before to give the mixture of alkenes (95%).

## 1-Chloro-1-phenysulfonylmethylcyclopropane 6a

Benzenesulfonyl chloride (4.01 g, 22.7 mmol) and AIBN (1.19 g, 7.1 mmol) were added to a solution of methylenecyclopropane (1.53 g, 28.4 mmol) in benzene (8 mL). The mixture was kept at 64°C (sealed tube) for 72 h, and concentration of the solution gave a brown oil, which was dissolved in pyridine, cooled to 0°C, treated with water (15 mL), and extracted with dichloromethane. The extracts were washed with dilute HCl and water to give a yellow oil (890 mg), which on flash chromatography gave the sulfone (218 mg., 0.94 mmol.), mp 64.5–66.0°C. $^1$H NMR ($CDCl_3$) $\delta$ 7.95 (d, 2H, $J = 8.5$ Hz), 7.70–7.55 (m, 3H), 3.45 (s, 2H), 1.15–1.10 (m, 2H), 1.05–1.00 (m, 2H). IR cm$^{-1}$ 1326, 1151 (s). MS: $(M+NH_4)^+$ 248. Found: C, 52.3; H, 4.8; Cl, 15.2; S, 13.9. $C_{10}H_{11}ClO_2S$ requires C, 52.1; H, 4.8; Cl, 15.4; S, 13.9%.

## 1-Bromo-1-phenylsulfonylmethylcyclopropane 6b

1-Bromomethyl-1-bromocyclopropane was obtained by the addition of bromine to methylenecyclopropane[23] at –80°C and had bp 70–74°C/20 mm. Hg. (lit.,[24] 60–70°C/15 mm, Hg). Thiophenol (2.6 mL, 25.9 mmol) in ethanolic sodium ethoxide (1 M, 26 mL, 26 mmol.) was added to the dibromide (26 mmol) in ethanol (5 mL). The mixture was refluxed for 2 h and was then quenched with water and extracted with dichloromethane. The extracts were washed successively with 2M sodium hydroxide and water, and evaporation gave the crude sulfide (5.7 g), of which (4 g) was dissolved in acetic acid (15 mL) at 60°C and treated dropwise with hydrogen peroxide (30%, 14 mL, 120 mmol). The cold mixture was diluted with saturated brine and extracted with dichloromethane. The extracts were washed with aqueous saturated sodium hydrogen carbonate and water. Evaporation gave the sulfone (4.18 g), which on crystallization from ethanol had mp 52.5–54.0°C (1.79 g). NMR $^1$H ($CDCl_3$) $\delta$ 8.00 (d, 2H, $J = 8.5$ Hz), 7.70–7.55 (m, 3H), 3.50 (s, 2H), 1.20–1.15 (m, 2H), 1.10–1.05 (m, 2H). MS: $M^+$ 275. Found: C, 43.8; H, 4.0; Br, 29.0; S, 11.6. $C_{10}H_{11}BrO_2S$ requires C, 43.7; H, 4.0; Br, 29.0; S, 11.7%.

## 4-Phenylsulfonylmethylenecyclopropane 7

Triethylamine (10.7 mmol) was added to 1-bromo-1-phenylsulfonylmethylcyclopropane **6b** (1.02 g, 4.34 mmol) in toluene (20 mL) at 25°C. After reflux for 48 h, the mixture was quenched with saturated aqueous ammonium chloride, and extraction with dichloromethane gave the sulfone (525 mg, 62%), mp 77–77.5°C. $^1$H NMR $\delta$ 7.90 (d, 2H, $J =$ 8.5 Hz), 7.65–7.50 (m, 3H) 6.75 (s, 1H), 1.60–1.45 (m, 2H), 1.40–1.25

(m, 2H). IR cm$^{-1}$ 1317, 1147 (s). MS M$^+$ 194 Found: C, 61.7; H, 5.2; S, 16.4. $C_{10}H_{10}O_2S$ requires C, 61.9; H, 5.2; S, 16.5%.

## Reaction of 4-Phenylsulfonylmethylenecyclopropane with Ethanolic Sodium Ethoxide

The methylenecyclopropane (50 mg, 0.26 mmol) in ethanol (20 mL) was treated with sodium ethoxide (2.6 mmol). The mixture was boiled under reflux for 12 h, quenched with saturated aqueous ammonium chloride, and extracted with dichloromethane. Evaporation of the extracts gave 1-ethoxy-1-phenylsulfonylmethylcyclopropane (48 mg, 81%), mp 114.5–116.5°C. $^1$H NMR ($CDCl_3$)$\delta$ 8.00 (d, 2H), 7.60–7.50 (m, 3H), 3.35 (s, 2H), 3.20 (q,2H), 0.90–0.75 (m, 5H), 0.60–0.55 (m, 2H). IR cm$^{-1}$1308, 1155 cm$^{-1}$ (s). MS: $(M+NH_4)^+$ 258 Found: C, 59.7; H, 6.9; S, 13.2. $C_{12}H_{16}O_3S_2$ requires C, 60.0; H, 6.7; S, 13.3%.

## 1-Phenylsulfonyl-1-phenylthiomethylcyclopropane 8

Methylenecyclopropane **6b** (483 mg, 2.5 mmol) in ethanol (15 mL) was treated with thiophenol (5 mmol) and sodium ethoxide (2.5 mmol). The mixture was refluxed for 4 h and quenched with water and extracted with dichloromethane. The extracts were washed successively with aqueous 5% sodium hydroxide and water. Evaporation gave the crude sulfide which was purified by HPLC to give the sulfide (550 mg, 73%). $^1$H NMR $\delta$ 7.95 (d, 2H, $J = 8.5$ Hz), 7.70–7.55 (m, 3H), 7.30–7.20 (m, 5H), 3.35 (s, H), 1.30–1.20 (m, 2H). IR cm$^{-1}$1319, 1151 (s). MS: M$^+$ 304. Found: C, 63.1; H, 5.4; S, 21.3. $C_{16}H_{16}O_2S_2$ requires 62.1; H, 5.3; S, 21.1%.

## 1-Phenylsulfonylmethyl-1-phenylsulfonylcyclopropane 9

The preceding sulfide **6b** (2.9 g, 5.6 mmol) was kept at 60°C in acetic acid (15 mL) while 30% hydrogen peroxide (8 mL, 70 mmol) was added dropwise. After 3 h, the mixture was diluted with cold brine and extracted with dichloromethane. The extracts were washed with saturated aqueous sodium hydrogen carbonate and water. Evaporation gave the sulfone (61%), mp 81.5–82.5°C from ethanol. $^1$H NMR ($CDCl_3$)$\delta$ 7.85–7.75 (m, 4H), 7.70–7.65 (m, 2H), 7.60–7.50 (m, 4H), 3.60 (s, 2H), 1.75–1.70 (m, 2H), 1.70–1.65 (m, 2H). IR cm$^{-1}$1321, 1147 cm$^{-1}$(s). MS: $(M+NH_4)^+$ 354. Found: C, 57.0; H, 4.7; S, 19.2. $C_{16}H_{18}O_4S_2$ requires C, 57.1; H, 4.8; S, 19.1%.

## Reaction of 1-Phenylsulfonylmethyl-1-phenylsulfonylcyclopropane 9 with Sodium Ethoxide and Piperidine

Piperidine (1.63 mmol) and sodium ethoxide (0.75 mmol) were added to the sulfone (100 mg, 0.3 mmol) in ethanol (10 mL) at 25°C. After 90 min, the mixture was quenched with saturated aqueous sodium chloride and extraction gave the piperidino-sulfone (**10**) (70 mg, 84%), mp 67.5–68.5°C. $^1$H NMR ($CDCl_3$) $\delta$ 7.85 (d, 2H, $J = 8.5$Hz), 7.60–7.45 (m, 3H), 3.45 (s, 2H), 2.40–2.35 (m, 4H), 1.30 (s, 6H), 0.9–0.80 (m, 2H), 0.80–0.45 (m, 2H). IR cm$^{-1}$ 1308, 1151 (s) MS $(M+H)^+$ Found: C, 64.5; H, 7.5; N, 4.9; S, 11.5. $C_{15}H_{21}NO_2S$ requires C, 64.5; H, 7.6; N, 5.0; S, 11.5%). When the experiment was repeated without addition of sodium ethoxide, the starting sulfone (92%) was recovered.

## 1-Ethoxy-1-phenylsulfonylmethylcyclopropane 11, R=OEt

The bromosulfone **6b** (1.01 g, 2.7 mmol) in ethanol (20 mL) was treated with sodium ethoxide (3 mmol). After 12 h at reflux, the mixture was quenched with aqueous ammonium chloride and extracted with dichloromethane. Evaporation of the extracts gave the sulfone (81%), mp 114.5–116.5°C (from ethanol). $^1$H NMR ($CDCl_3$) $\delta$ 8.00 (d, 2H, $J =$ 8.5 Hz)), 7.60–7.50 (m, 3H), 7.60–7.50 (m, 4H), 3.35 (s, 2H), 3.20 (q, 2H, $J = 6.2$ Hz), 0.90–0.75 (m, 5H), 0.60–0.55 (m, 2H). IR cm$^{-1}$ 1308, 1155 cm$^{-1}$ (s). MS: $(M+NH_4)^+$ 258. Found: C, 59.7; H, 6.9; S, 13.2 $C_{12}H_{16}O_3S$ requires C, 60.0; H, 6.7; S, 13.3%.

## 1-Methoxy-1-phenylsulfonylmethylcyclopropane 11, R=OMe

The bromosulfone **6b** (694 mg, 2.5 mmol) in methanol (20 mL) was treated with sodium methoxide (19 mmol). After 12 h at reflux, the mixture was treated as above to give the sulfone (74%), mp 71–72°C (from ethanol). $^1$H NMR ($CDCl_3$) $\delta$ 7.95 (d, 2H, $J = 8.5$Hz), 7.55–7.40 (m, 3H), 3.30 (s, 2H), 2.95 (s, 3H)), 0.80–0.75 (m, 2H), 0.50–0.45 (m, 2H). IR cm$^{-1}$ 1308, 1152 cm$^{-1}$ (s). MS $(M+H)^+$ 227 Found: C, 58.2; H, 6.2; S, 14.2. $C_{11}H_{14}O_3S$ requires C, 58.4; H, 6.2; S, 14.2%.

## Reaction of Phenylsulfonylmethylcyclopropane (6, Hal=H) with Ethanolic Sodium Ethoxide

The sulfone[25] (50 mg) was treated with 0.5 M ethanolic sodium ethoxide (5 mL), and the mixture was kept in a sealed tube for 24 h at 150°C and then quenched and extracted as before to give recovered sulfone (48 mg, 96%).

### Product Analyses

These were conducted as for 4-phenylsulphonylmethylenecyclopropane above. Results are in Table II.

### Kinetics

Solutions of ethanolic sodium ethoxide were prepared by dissolution of clean sodium in dry ethanol and were standardized against hydrochloric acid. For reactions followed by UV spectroscopy, substrates were used at concentrations of $10^{-3}$–$10^{-4}$ M; concentrations of base were 10 to 100 times greater. For reactions followed by gc, sealed tubes were used, and samples were quenched with aqueous ammonium chloride and extracted with dichloromethane.

### Labeling Studies

Solutions of sodium ethoxide in deuterioethanol were used so as to have a base-substrate ratio of 0.5:1. Work-up was the same as for the product analyses. Deuterium incorporation was measured by $^2$H NMR. Incorporation results are in Table II.

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