Tetrahedron. Vol 30, pp. 3883 to 3890 Pergamon Press 1974. Printed in Great Britain

THE [2, 3]-SIGMATROPIC REARRANGEMENT OF PROPARGYL BENZENESULPHINATES TO ALLENYL PHENYL SULPHONES[1,a]

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(*Received in the UK 8 May 1974; Accepted for publication 15 June 1974*)

Abstract—α-Methyl-, α-phenyl-, α,α-dimethyl-, and α-ethyl-α-methylpropargyl benzenesulphinates were found to undergo thermal rearrangement in high yields to sulphones, accompanied by a simultaneous acetylene-allene isomerization. The allenic sulphones produced by the rearrangement of the α-monosubstituted propargyl esters underwent further rearrangement under the reaction conditions, to γ-substituted propargyl phenyl sulphones, by way of a base-catalyzed [1,3] - prototropic shift. A kinetic study of the rearrangement reaction was carried out using two different esters. This study revealed that the rearrangement exhibited a relatively low sensitivity to the effect of solvent ionizing power and substituents. These data and other pertinent evidence suggest a concerted [2,3] - sigmatropic rearrangement.

In view of the vast amount of interesting work on allene chemistry,[3] it is not surprising that acetylene-allene rearrangements have also been studied extensively in the past.[4] Taylor[3c] has classified this type of isomerization into four mechanistically distinct groups, prototropic, anionotropic, displacement and intramolecular propargylic rearrangements. The present work is related to the last type, which can be further subdivided into [3,3] and [2,3] sigmatropic rearrangements,[5] or according to an older terminology, into "six- and five-membered transition state" processes.

The Claisen-type rearrangement of propargyl vinyl ethers to β-allenic aldehydes[6] shows considerable stereospecifity[6b] and has been interpreted by Landor[6a] to proceed by a concerted [3,3] - sigmatropic transformation. Similarly, Baldwin and Walker[7] have observed a Reformatsky-Claisen reaction of propargylic α - bromocarboxylates to β - allenic acids, and have suggested that it takes place by a [3,3] - sigmatropic rearrangement of the intermediate zinc enolate. The allied Cope-type rearrangement of diethyl isobutenylpropargylmalonate to diethyl 2,2 - dimethylpenta - 3,4 - dienylidenemalonate has also been reported by Landor.[8] The rearrangement of propargyl carboxylates to the corresponding allenyl esters has been investigated by several groups.[9] Landor[9a] has reported the conversion in high yield of 1 - ethynyl - 2,2,6,6 - tetramethylcyclohexyl acetate to 2,2,6,6 - tetramethylcyclohexylidenevinyl acetate under pyrolytic conditions, and suggested a cyclic intramolecular mechanism. Saucy, Marbet and coworkers[9b] have utilized this type of reaction for the preparation of α,β-unsaturated aldehydes. Recently, Schmid and coworkers[9c] have published a detailed study on the mechanism of the catalysis of the reversible rearrangement of propargyl benzoates to the corresponding allenyl esters by silver(I) ions, using optically active esters as well as ^{14}C and ^{18}O - labelling, and concluded that the process can be described as a [3s,3s] - sigmatropic reaction occuring in a silver - π - complex with the triple bond in the first ester and with a C,C double bond in the allenyl ester. A somewhat similar rearrangement is that of propargylic chlorosulphinates to allenyl chlorides, accompanied by extrusion of sulphur dioxide.[10]

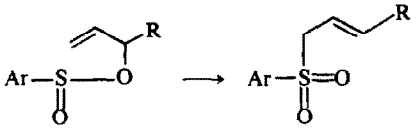
The [2,3] - sigmatropic rearrangement of propargylic systems has been studied to a smaller extent so far. Propargyl phosphinites and propargyl phosphites have been reported to undergo spontaneous isomerization to allenyl phosphine oxides and allenyl phosphonates, respectively.[11] Similarly, propargyl trichloromethanesulphenates[12] and *p*-toluenesulphenates[2b] have been found to undergo spontaneous rearrangement to allenyl trichloromethyl and allenyl *p*-tolyl sulphoxides, respectively. As an extension of this work, propargyl sulphoxylates have been observed[13] to rearrange to propargyl allenesulphinates, also spontaneously. Recently, propargylic sulphonium ylids have been shown to undergo [2,3] - sigmatropic rearrangement to β - allenic sulphides.[14] All these reactions have been suggested to proceed by cyclic intramolecular mechanisms.

Turning now to the rearrangement of esters of arenesulphinic acids,[15] one finds that it has received considerable attention in the past. Kenyon and coworkers[16] reported that the rearrangement of α - phenylethyl *p* - toluenesulphinate to the

[a] Dedicated to the memory of the late Professor David Darwish of the University of Alberta, Edmonton, Alberta.

corresponding sulphone was favoured by an increase in solvent polarity, and that in formic acid the optically active ester was converted to completely racemic sulphone. These results were considered as consistent with an ionic mechanism. Wragg and coworkers[17] investigated the rearrangement of a number of sulphinates to sulphones and suggested an intermolecular ionic mechanism for their results. More recently Darwish and coworkers[18] have examined the rearrangement of t-butyl, benzhydryl, α-phenylethyl and trityl arenesulphinates under various conditions and have shown that the important route to sulphone formation is ion-pair recombination, and not recombination of free ions. A similar interpretation has been advanced for the rearrangement of benzyl benzenesulphinates.[19]

The rearrangement of allylic arenesulphinates proceeds by a different mechanism. This rearrangement was first studied by Cope, Morrison and Field,[20] but these authors have reached no final decision with regard to mechanism. A subsequent study by Darwish and Braverman[21] of this system revealed some unique features. Even under solvolytic conditions these esters undergo rearrangement in high yield to sulphone, and the rearrangement of unsymmetrically substituted allylic esters involves simultaneous isomerization of



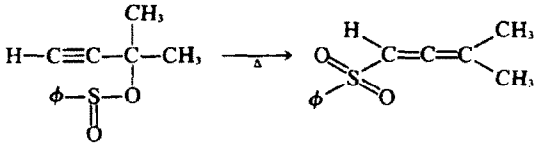
the allylic group. A kinetic study of the rearrangement indicated relatively low sensitivity of the rate to the nature of the substituent and solvent. On the basis of these observations and other pertinent data, it has been suggested[21] that the rearrangement to sulphone proceeds by a cyclic intramolecular mechanism, that is, by a concerted [2,3]-sigmatropic shift.[5b]

This rearrangement has been used by us as a model for the prediction of a number of related rearrangements. Recently, we have reported the analogous rearrangements of allylic[22] and propargylic[12] trichloromethanesulphenates to allylic and allenic trichloromethyl sulphoxides, respectively. We now wish to present a full report of our results on another natural extension, namely the rearrangement of propargyl benzenesulphinates to allenyl phenyl sulphones.

RESULTS AND DISCUSSION

This investigation was initiated by an examination of the thermal behaviour of α,α-dimethylpropargyl benzenesulphinate, which was prepared by reaction of the corresponding alcohol with benzenesulphinyl chloride in pyridine at low temperature. The protons of the two methyl groups of this ester are diastereotopic,[23] and show two singlets in the NMR at τ8·33 and 8·20. This information is useful in the characterization of this type of compound. α,α - Dimethylpropargyl benzenesulphinate was found to readily undergo thermal rearrangement to γ,γ - dimethylallenyl phenyl sulfone (Eq 1), thus indicating the occurrence of a simultaneous "1,3 - allylic shift" for this system also, in spite of certain geometrical differences. Reaction conditions and yields are summarized in Table 1.

The sulphone is formed in high yields even in hydroxylic solvents. Titrimetric measurements show that solvolysis by alkyl-oxygen bond fission does not occur in ethanol or 80% ethanol - water mixture, while in acetic acid slight solvolysis (3%) may take place. These results contrast with those



(1)

Table 1. Rearrangement of α,α-dimethylpropargyl benzenesulphinate to γ,γ-dimethylallenyl phenyl sulphone

Solvent	[Ester],M	Buffer	[Buffer],M	Time h	Temp. °C	Sulphone yield(%)
Acetic acid[a]	0·1398	NaOAc	0·3172	21	70	91·0
Ethanol	0·0523	2,6-Lutidine	0·1009	19	78	85·0
80% Ethanol-water	0·0433	2,6-Lutidine	0·0866	5	75	85·3
Acetonitrile	0·0952	2,6-Lutidine	0·2813	12	80	88·1
Chloroform	0·1800	K_2CO_3	—	23	75	100

[a] In this solvent 3% of acid was produced. No acid was detected in the other solvents.

observed for the rearrangement of benzhydryl,[18a] *p*- anisyl[19] and furfuryl[24] arenesulphinates to their corresponding sulphones, which is accompanied by considerable solvolysis, and which is believed to proceed by an ionization and ion-pair recombination mechanism.

It is well known that the driving force for the sulphinate to sulphone isomerization is the formation of the strong sulphur - oxygen bond in the sulphonyl group (112 kcal/mole),[25] as a result of back donation of a pair of nonbonding electrons from the oxygen atom into empty d orbitals of the sulphur atom, with consequent $p_\pi - d_\pi$ overlap.[26] As is evident from the diagram shown in Fig 1, which was devised by Moore[27] and which interrelates the energies of isomeric acyclic acetylenes and allenes, a terminal allene is lower in energy by 0·9 kcal/mole than an isomeric terminal acetylene, while a nonterminal allene is still lower in energy. Accordingly, the isomerization of a terminal acetylenic sulphinate to a nonterminal allenic sulphone, as observed in the present case, is favoured on thermodynamic grounds.

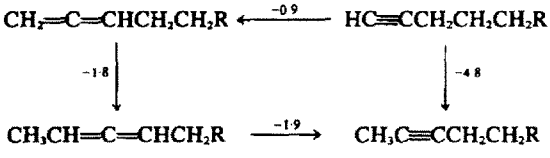
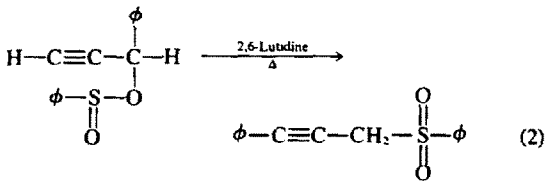


Fig. 1. Approximate standard enthalpies in kcal/mole of isomerization of gaseous acetylenes and allenes at 25° (taken from Ref. 27).

In principle, the rearrangement of the propargylic sulphinate to allenic sulphone could take place by either an ionic or concerted mechanism. However, the observation of complete acetylene - allene isomerization, as well as the practically complete absence of solvolysis suggest the operation of a cyclic intramolecular (i.e. a concerted [2,3] sigmatropic shift[5b]) mechanism for the rearrangement of ester to sulphone, reminiscent of the mechanism of rearrangement of allylic sulphinates[21] and sulphenates[22] to sulphones and sulphoxides, respectively. Further support for this mechanism is provided in the present study.

As expected, the reaction of α - ethyl - α - methylpropargyl benzenesulphinate is quite analogous to that of the corresponding dimethyl ester, just described. For example, it was found to rearrange in quantitative yield to γ - ethyl - γ - methylallenyl phenyl sulphone on heating in ethanol for 14 hours at 75°, under buffered conditions. On the other hand, somewhat different behaviour has been observed with the secondary, α - methyl- and α - phenylpropargyl benzenesulphinates. The rearrangement of these esters to allenic sulphones was generally accompanied by the formation of additional products, and under certain conditions the allenic sulphone was not detected at all. Thus, on heating the α - phenylpropargyl ester for 6 h at 80° in acetonitrile, in the presence of 2,6 - lutidine, it rearranged to γ - phenylpropargyl phenyl sulphone in 94% yield (Eq 2). In the same solvent, but in the absence of base,



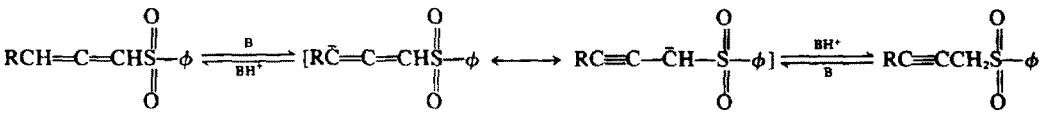
(2)

heating for 4·7 hours at 75°, yielded the expected γ-phenylallenyl phenyl sulphone together with a small quantity of α-phenylpropargyl phenyl sulphone. 12% of acid and some phenyl benzenethiosulfonate were formed, apparently resulting from liberated benzenesulphinic acid[15a].

Similarly, on refluxing a solution of α-methylpropargyl benzenesulphinate in ethanol for 32 hours, in the presence of 2,6 - lutidine, the main product was ethyl benzenesulphinate together with γ - methylpropargyl phenyl sulphone. The formation of the transesterification product, ethyl benzenesulphinate, is explained by competing base catalyzed solvolysis involving sulphur-oxygen bond fission,[28] facilitated by the lower reactivity of this ester with respect to the sigmatropic shift. On the other hand, heating the ester in acetonitrile for 182 hours at 75°, in the absence of any base, gave γ-methylallenyl phenyl sulphone and phenyl benzenethiosulphonate in a ratio of 1·3 : 1. A little terminal acetylenic sulphone was also formed under these conditions. Finally, heating the ester in chloroform solution for 85 hours at 90° over calcium carbonate, yielded a mixture of γ-methylallenyl (57%) and γ - methylpropargyl (43%) phenyl sulphones, while heating in acetonitrile under similar conditions, again over calcium carbonate, gave only the first product, in almost quantitative yield.

From these results it appears that the secondary propargylic sulphinates are likely to undergo rearrangement to allenic and/or nonterminal acetylenic sulphones. And in the absence of base terminal acetylenic sulphones, as well as "solvolysis" products, are also formed, apparently, by acid catalyzed ionic pathways. The γ - phenyl- and γ - methylpropargyl phenyl sulphones are most likely formed from their allenic isomers *via* a base catalyzed prototropic shift (Eq 3).

Supporting evidence for this interpretation is provided by the observation that in the presence of 2,6 - lutidine only the internal acetylenic sulphones are formed, while under similar conditions, but in the absence of base, the expected allenic sulphones



(3)

are obtained. Likewise, in the presence of calcium carbonate, as a heterogeneous phase which limits catalysis of proton transfer, allenic sulphones, alone or together with their isomerization products, are obtained. Further evidence for this explanation is found in the fact that γ-methylallenyl phenyl sulphone isomerizes almost completely to γ-methylpropargyl phenyl sulphone on heating in acetonitrile for 18 hours at 75°, in the presence of 2,6 - lutidine. These results are also consistent with the thermodynamic data shown in Fig 1, which indicate that a nonterminal acetylene is more stable than an isomeric nonterminal allene by 1·9 kcal/mole. In the present case, the stabilization energy is expected to be lower due to the conjugation present in the allenic sulphone. A similar interconversion of γ-methylallenyl phenyl sulphone to its γ-methylpropargyl isomer was observed by Smith and Stirling,[2b] during purification of the first sulphone on neutral alumina. Since this observation contrasts with those on the three carbon series earlier investigated by Stirling,[29] it has been concluded[2b] that the following order of thermodynamic stabilities applies; nonconjugated nonterminal acetylene > conjugated allene > conjugated nonterminal acetylene > nonconjugated terminal acetylene. Other examples of alleneacetylene interconversions can be found in the literature.[30]

A kinetic study of the [2,3] - *sigmatropic rearrangement.* In order to gain further information with regard to the mechanism of rearrangement of propargylic sulphinates to the allenic sulphones a kinetic study of the reaction was undertaken, with special attention to the effect of the ionizing power of the solvent and the substituent on the rate of rearrangement. The first-order rate constants for disappearance of α-methyl- and α,α-dimethylpropargyl benzenesulphinates, under various conditions, are presented in Table 2.

Examination of the data of Table 2, indicates that the rate of rearrangement of the α,α - dimethylpropargyl ester to sulphone is enhanced by increase in the ionizing power of the solvent, which would suggest a polar transition state. However, the size of the solvent effect in this case is strikingly smaller than that observed for reactions taking place by an ionization mechanism. For example, while the rate of rearrangement of benzhydryl 2,6 - dimethylbenzenesulphinate to the corresponding sulphone at 90° is 33·3 times faster in acetic acid than in ethanol,[18a] the rate of rearrangement of α,α - dimethylpropargyl benzenesulphinate is only faster by a factor of 1·4. Similarly, while the rate of ionization of *p*-methoxyneophyl tosylate at 75° is 52 times faster in 80% ethanol - water than in acetonitrile,[31] a factor of only 3·2 is noted for the same change in solvents in the present case. Consequently, it is evident that the change in charge separation between the ground state and the transition state is drastically smaller than for an ionization process.

In order to test the solvent effect in a more quantitative fashion, we have used Eq 4, suggested by Smith, Fainberg and Winstein[31]

$$\log k_{reaction} = a \log k_i + b \qquad (4)$$

where $k_{reaction}$ and k_i are the rate constants of the reaction being examined and that of ionization of *p*-methoxyneophyl tosylate, respectively. The a value in the above equation, which can be obtained

Table 2. Rate constants[a] for the rearrangement of propargylic benzenesulphinates to allenyl phenyl sulphones

Benzene-sulphinate	Solvent	Temp. °C	[Ester],M	[Base],M	$10^4 k$, sec^{-1}
α,α-Dimethyl-propargyl	Acetonitrile	75	0·0536	0·1136[b]	1·11 ± 0·02
	Ethanol	75	0·0520	0·1328[b]	2·10 ± 0·10
	Acetic acid	75	0·0536	0·1072[c]	2·96 ± 0·13
	80% Ethanol	75	0·0528	0·1258[b]	~3·5
	Acetonitrile	60	0·0484	0·0940[b]	0·224 ± 0·017
	Chloroform	90	0·0533	—[d]	5·30 ± 0·19
	Acetonitrile[e]	90	—	—	4·80
α-Methyl-propargyl	Acetonitrile	90	0·0933	—[f]	0·196 ± 0·010

[a] Determined by infrared spectroscopy (see Experimental). [b] 2,6 - Lutidine. [c] Sodium acetate. [d] Calcium carbonate, 55 mg/ml. [e] Extrapolated from lower temperatures. In this solvent, $\Delta S^* = -12·8$ e.u. [f] Calcium carbonate, 90 mg/5 ml.

graphically, was suggested by these authors as a measure of relative sensitivity of a reaction to the ionizing power of the solvent. As illustrated in Fig 2, log k for rearrangement of α,α - dimethylpropargyl benzenesulphinate, using 80% ethanol - water, acetic acid, ethanol and acetonitrile as solvents at 75°, correlated quite well with log k for ionization of *p*-methoxyneophyl tosylate in the same solvents and temperatures. The slope of the straight line is 0·28. From the magnitude of the a value thus determined, it is clear that the rearrangement of α,α - dimethylpropargyl benzenesulphinate exhibits a low sensitivity to variation in solvent ionizing power, which is of the same order as that observed for the rearrangements of allylic 2,6 - dimethylbenzenesulphinates,[21] thionbenzoates[32] and azides[33] (a = 0·19, 0·15 and 0·12, respectively), believed to proceed by a cyclic intramolecular mechanism.

The negative value of the entropy of activation (ΔS^* −12·8 e.u.) obtained for the reaction of α,α - dimethylpropargyl benzenesulphinate in acetonitrile tends to support a highly ordered transition state, consistent with the operation of a concerted mechanism for the rearrangement. In order to determine the substituent effect, the rates of rearrangement of α,α-dimethylpropargyl benzenesulphinate in acetonitrile at 90°, was compared with that of the corresponding α-methylpropargyl ester, under identical conditions. As shown by the data of Table 2, the reaction of the first ester is 23 times faster than that of the second one. The magnitude of the effect of substitution of an α-hydrogen by a methyl group, thus determined, is much smaller than the effect produced by such a substitution in systems reacting by ionization mechanisms. For example, it has been reported[34] that the solvolysis of α,α,γ - trimethylpropargyl chloride in 80% ethanol is faster than that of α,α - dimethylpropargyl chloride by a factor of three powers of ten, and one may assume that an α - methyl group may have an even greater effect. Similarly, for the ionization of allylic chlorides,[35] substitution by an α-methyl group enhances the rate by three powers of ten. Consequently, the small magnitude of the substituent effect on the reactivity of the propargylic sulphinates may be considered as indicative of relatively little charge separation in the transition state, consistent with a cyclic intramolecular mechanism. These results resemble those observed for the rearrangement of allylic arenesulphinates[21] and thionbenzoates,[32] for which a parallel interpretation has been advanced.

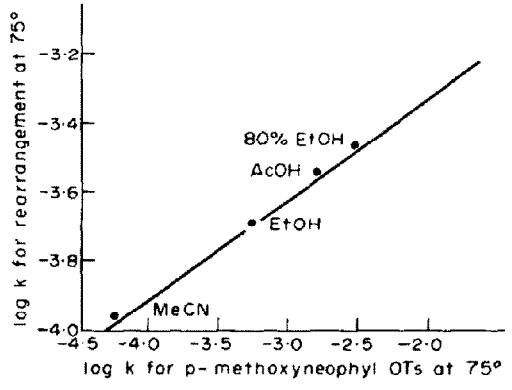


Fig 2. Plot of log. k for rearrangement of α,α - dimethylpropargyl benzenesulphinate vs. log. k for ionization of *p*-methoxyneophyl tosylate at 75°. Slope 0·28.

The data presented in this report bear a close relationship to the data previously reported on the spontaneous isomerization of propargylic trichloromethanesulphenates[12] and sulphoxylates[13] at low temperatures to allenyl trichloromethyl sulphoxides and propargyl allenesulphinates, respectively. The great enhancement in the rate of rearrangement of the last two systems relative to the propargylic sulphinates can be reasonably ascribed to the greater nucleophilicity of the sulphur atom in the first compounds. This observation may also be used in support for a cyclic mechanism. In conclusion, and in the light of the evidence presented above, it is suggested that the rearrangement of propargylic sulphinates to allenyl sulphones proceeds by a concerted [2,3] - sigmatropic shift[5b] mechanism.

Our observations on the rearrangement of propargylic benzenesulphinates are confirmed by the work of Stirling and coworkers,[2] performed contemporaneously with ours. These authors report that γ - deuteriopropargyl *p*-toluenesulphinate rearranged to α-deuterioallenyl *p*-tolyl sulphone on heating in chlorobenzene at 130°, and that under similar conditions R(+) - α - methylpropargyl *p* - toluenesulphinate rearranged to (−) - γ - methylallenyl *p*-tolyl sulphone whose absolute configuration, predicted on the basis of a cyclic intramolecular mechanism, agrees with that calculated from the polarizability sequence of substituents attached to the allene system.

The present work has laid the ground for the facile preparation of diallenic sulphones which have been found to undergo a novel cyclization to thiophene - 1,1 - dioxides, a reaction of considerable mechanistic interest as well as synthetic utility.[13]

EXPERIMENTAL

Melting points and boiling points are uncorrected. Refractive indeces were measured by means of a Bausch and Lomb, Model Abbe-3L Refractometer. Infrared spectra were recorded on a Beckman IR5, or a Perkin Elmer Model 237, spectrophotometer, using 0·1 mm NaCl cells and chloroform as solvent, unless otherwise indicated. All the kinetic measurements were made on the first instrument. Nuclear magnetic resonance spectra were recorded on a Varian A-60 spectrometer, using

$CDCl_3$ as solvent and TMS as internal standard. Ultraviolet spectra were taken on a Bausch and Lomb Spectronic 505 spectrophotometer. Microanalyses were done at the Microanalytical Laboratory of the Weizmann Institute of Science at Rehovot.

Solvents and Materials. Anhydrous ethanol was dried by the method of Lund and Bjerum as described by Fieser,[36a] and contained not more than 0·045% of water, as determined by a Karl Fischer titration. X% ethanol-water means a solution prepared by mixing X volumes of ethanol with (100-X) volumes of distilled water at 25°. The same pipette was used for measuring all volumes. Acetic acid was dried by the method described by Fainberg and Winstein,[37] and contained 0·1M of acetic anhydride. Acetonitrile was purified by the method described by Smith, Fainberg and Winstein,[31] and contained less than 0·0075% of water. Chloroform was purified by the method suggested by Fieser.[36b] Benzene and chlorobenzene were dried by means of anhydrous calcium chloride, and the first solvent also by means of sodium, followed by distillation.

2,6 - Lutidine was refluxed over, and distilled from, barium oxide (b.p. 140–142°). The propargylic alcohols used were of Fluka (puriss) grade and were distilled before use. In the case of α-methylpropargyl alcohol, which is sold as a 55% aq. solution, the alcohol was first extracted with ether, after addition of NaCl, and the ether subsequently removed. Benzenesulphinic acid was prepared by reduction of benzenesulphonyl chloride with sodium bisulphite as described by Krishna and Singh[38] (yield 82%) m.p. 83–4° (lit. 85°). The acid was stored in the freezer before use. Benzenesulphinyl chloride was prepared from the corresponding acid as described by Darwish and Noreyko[28] (yield 98%).

Preparation of sulphinates. α,α - Dimethylpropargyl benzenesulphinate. To a solution of 16·05 g (0·10 mole) of benzenesulphinyl chloride in 30 ml of dry pyridine, cooled in a dry ice-acetone bath, was gradually added a cold solution of 7·99 g (0·095 mole) of α,α - dimethylpropargyl alcohol in 10 ml of dry pyridine. After an hour the cooling bath was removed and the reaction mixture allowed to stand for an additional hour at room temperature. The product was extracted with 300 ml of ether and washed with 100 ml portions of 2N HCl, 10% $NaHCO_3$, and several times with water. After drying over anhydrous magnesium sulphate and evaporation of the ether at the water aspirator, 13·1 g (66% yield) of the ester were obtained, m.p. 36–7° (from pentane). The ester must be stored in the freezer, because of decomposition at room temperature. It showed infrared absorption peaks at 3300 and 2125 cm^{-1}, characteristic of the ethynyl group,[39a] and at 1146, 1122, 952 and 857 cm^{-1}, due to the sulphinate group.[39b] The NMR spectrum showed signals at τ 2·2–2·7 (5H, m), 7·14 (1H, s), 8·20 (3H, s) and 8·33 (3H, s). Calcd. for $C_{11}H_{12}O_2S$: C, 63·43; H, 5·81; S, 15·39; Found: C, 63·78; H, 6·00; S, 15·42%.

α - Ethyl - α - methylpropargyl benzenesulphinate was prepared by reaction of α - ethyl - α - methylpropargyl alcohol and benzenesulphinyl chloride, as described for the α,α-dimethyl analogue (yield 93%). The compound was purified by column chromatography on silica gel, using methylene chloride as eluent, n_D^{22} 1·5257. The infrared spectrum showed characteristic peaks at 3300, 2112, 1126 and 867 cm^{-1}, and the NMR spectrum showed signals at τ 2·10–2·61 (5H, m), 7·10 (1H, s), 8·08 (2H, m), 8·21 and 8·34 (3H, 2s) and at 8·91 and 8·96 (3H, 2t, J = 7 Hz). This compound, as well as the following two esters, consisted of a diastereomeric mixture of two racemates, which explains the NMR spectral data.

α-Phenylpropargyl benzenesulphinate, was prepared from α-phenylpropargyl alcohol and benzenesulphinyl chloride, as described for the α,α-dimethylpropargyl ester (yield 72%). The ester was purified by crystallization from pentane at −70°, but it melts at room temperature, n_D^{22} 1·5854. Its infrared spectrum showed characteristic IR peaks at 3295, 2121, 1133, and 900 cm^{-1}, and its NMR spectrum displayed a multiplet at τ 2·22–2·87 (10 H), two doublets at τ 4·05 and 4·09 (1H, J = 2·4 Hz) and two doublets at 7·03 and 7·40 (1H, J = 2·4 Hz).

α-Methylpropargyl benzensulphinate, was prepared from α-methylpropargyl alcohol and benzenesulphinyl chloride as described for the corresponding α,α-dimethylpropargyl ester, and was purified by means of active carbon, $n_D^{25} = 1·5423$ (yield 91%). The compound showed characteristic IR peaks at 3297, 2120, 1127 and 895 cm^{-1}, and NMR signals at τ 2·23–2·67 (5H, m), 5·04 (1H, m), 7·39 and 7·57 (1H, 2d, J = 2·3) and 8·44 and 8·50 (3H, 2d, J = 6·6 Hz).

Rearrangement of sulphinates to sulphones. Rearrangement of α,α-dimethylpropargyl benzenesulphinate. Solutions of the ester and base in the appropriate solvents were prepared and heated in sealed ampoules in a constant temperature bath, or refluxed for the time periods and at the temperatures specified in Table 1. After cooling to room temperature, a 5 ml sample of the solution was titrated with a solution of sodium methoxide in methanol, using phenolphthalein as indicator, except for the run in acetic acid for which the sample was titrated with a solution of $HClO_4$ in acetic acid, using crystal violet as indicator. In each case the results were compared with those obtained before heating the solution. No acid was produced in all the runs, except the run in acetic acid where the formation of 3% of acid was demonstrated. The reaction products were extracted with ether, and washed consecutively several times with water, dilute HCl, 10% $NaHCO_3$, and water again. After drying over anhydrous $MgSO_4$ the ether was removed and the IR and NMR spectra were recorded. For the reaction in chloroform, the solvent was evaporated directly, after filtration of the calcium carbonate which served as buffer. While in the case of acetic acid, a weak absorption in the IR also indicated presence of acetate ester, the only product detected in all the runs summarized in Table 1 was γ,γ-dimethylallenyl phenyl sulpone, m.p. 36–7° (from pentane), IR absorption peaks at 1960 (m) cm^{-1} characteristic of allenes,[40] and at 1148, 1312 and 1319 cm^{-1}, due to the sulphonyl group.[39c] The NMR spectrum displayed signals at τ 2·0–2·5 (5H, m), 3·93 (1H, septet, J = 2·8 Hz) and 8·23 (6H, d, J = 2·8 Hz). Calcd. for $C_{11}H_{12}O_2S$: C, 63·43; H, 5·81; S, 15·39; Found: C, 63·77; H, 5·82; S, 15·51%.

Rearrangement of α-ethyl-α-methylpropargyl benzenesulphinate. A 0·730 g (3·29 mmoles) quantity of the ester and 1·654 g (15·5 mmoles) of 2,6-lutidine were dissolved in 50 ml of ethanol. After titration of a 5 ml sample as described in the preceding paragraph, the rest of the solution was sealed in an ampoule and heated for 14 h at 75° in a constant temperature bath. No change in acidity was noted. After extraction of the products by the normal procedure, 0·650 g (yield 99%) of γ-ethyl-γ-methylallenyl phenyl sulphone was obtained, m.p. 70–71° (from pentane), IR absorption peaks at 1955, 1316, 1306, 1143 cm^{-1}, and NMR signals at τ 1·97–2·56 (5H, m), 3·81 (1H, sextet), 7·93 (2H, q, J = 7·1 Hz, with further splitting

of each line to a doublet) 8·22 (3H, d, J = 2·7 Hz) and 9·05 (3H, t, J = 7·1 Hz). Calcd. for $C_{12}H_{14}O_2S$: C, 65·12; H, 6·50; S, 14·24. Found: C, 64·82; H, 6·35; S, 14·42%.

Rearrangement of α-phenylpropargyl benzenesulphinate.

(a) A 2·264 g (8·84 mmoles) quantity of the ester and 2·370 g (22·1 mmoles) of 2,6-lutidine were dissolved in 100 ml of acetonitrile, and heated for 6 h at reflux temperature. After extraction of the products by the normal procedure, 2·142 g (94% yield) of γ-phenylpropargyl phenyl sulphone were obtained, m.p. 115–116° (from i-PrOH). The compound showed significant IR absorption peaks at 2221 cm^{-1} due to the acetylenic group and at 1134, 1163, 1309 and 1324 cm^{-1}, due to the sulphonyl group. Its UV spectrum showed absorption peaks at λ_{max} 218 nm (log ε 4·20), 2·41 nm (log ε 4·26) and 2·71 nm (log ε 3·34). The NMR spectrum showed two signals, at τ 1·87–2·69 (10H, m) and 5·80 (2H, s). Calcd. for $C_{15}H_{12}O_2S$: C, 70·05; H, 4·85. Found: C, 70·29, H, 4·72%.

(b) A 2·209 g (8·63 mmoles) quantity of the ester was dissolved in 50 ml of acetonitrile and heated in a sealed tube for 4·7 h at 75°. Titration of a sample at the end of the reaction indicated the development of 12% of acid. Extraction with ether gave a mixture of products weighing 2·124 g. From this mixture a yellowish solid was separated, which turned yellow at 112° and red at 170°. It showed IR absorption at 2125 and 3300 cm^{-1} characteristic of terminal acetylenes, and at 1133, 1154, 1314 and 1325 cm^{-1}, due to the sulfonyl group. The NMR spectrum displayed peaks at τ 2·36–2·65 (10H, m), 4·91 (1H, d, J = 2·8) and 7·33 (1H, d, J = 2·8). On the basis of these spectral data it was identified as α-phenylpropargyl phenyl sulphone. The rest of the material was separated by column chromatography using silica gel S (Fluka) with benzene as eluent. One compound thus obtained was phenyl benzenethiosulphonate, m.p. 44° (lit[41] 45–6°), IR peaks at 1080, 1149, 1313 and 1328 cm^{-1}, and an NMR multiplet at τ 2·35–2·72. The other compound was γ-phenylallenyl phenyl sulphone, IR peaks at 1149, 1310, 1325 and 1946 cm^{-1}, and NMR signals at τ 2·00–2·76 (10H, m), 3·28 (1H, d, J = 7·0 Hz), 3·33 (1H, d, J = 7·0 Hz).

Rearrangement of α-methylpropargyl benzenesulphinate.

(a) A 1·089 g (5·6 mmoles) quantity of the ester and 1·877 g (17·5 mmoles) of 2,6-lutidine were dissolved in 100 ml of dry ethanol and refluxed for 32 h. The solution, which became red colored, was extracted with ether as usual. The IR spectrum of the residue (0·940 g) indicated the presence of ethyl benzenesulphinate as the main product (strong peaks at 1128 and 885 cm^{-1}). The other product, γ-methylpropargyl phenyl sulphone, was separated by crystallization from pentane, m.p. 57–8°, IR peaks at 1132, 1149, 1163, 1307, 1321 and 2235 cm^{-1}, and NMR signals at τ 1·95–2·47 (5H, m), 6·08 (2H, q, J = 2·6 Hz), and 8·22 (3H, t, J = 2·6 Hz).

(b) A 1·440 g (7·42 mmoles) quantity of the ester was dissolved in 50 ml of acetonitrile, sealed in an ampoule and heated for 182 h at 75°. The solution turned brownish-red. Extraction with ether in the usual manner yielded 0·972 g of material which consisted of a mixture of γ-methylallenyl phenyl sulphone (see spectral data below), and phenyl benzenethiosulphonate in the ratio 1·3:1.

(c) A solution of 0·205 g (1·1 mmole) of the ester in 10 ml of acetonitrile was heated in a sealed ampoule for 119 h at 90°, in the presence of 0·161 g of calcium carbonate. After filtration of the carbonate and removal of the solvent under reduced pressure 0·204 g (~ 100% yield) of γ-methylallenyl phenyl sulphone was obtained as a colorless liquid, IR peaks at 1145, 1308, 1316 and 1957 cm^{-1}, and NMR signals at τ 2·00–2·50 (5H, m), 3·84 (1H, q, J = 3·0 Hz), 4·18 (1H, q, J = 7·3 Hz) and 8·23 (3H, d, J = 7·3 Hz). Each line of the last three signals is further split into two lines.

(d) A solution of 0·947 g (4·88 mmoles) of ester dissolved in 50 ml of chloroform was heated in a sealed tube for 85 h at 90°, in the presence of 0·840 g of calcium carbonate. After filtration of the carbonate and evaporation of the solvent 0·945 g (~ 100% yield) of a mixture of γ-methylallenyl and γ-methylpropargyl phenyl sulphones was obtained in the ratio of 6:4 as determined by NMR.

Isomerization of γ-methylallenyl to γ-methylpropargyl phenyl sulphone. To a solution of 0·107 g (0·55 mmole) of γ-methylallenyl phenyl sulphone in 10 ml of acetonitrile was added 0·107 g (1·0 mmole) of 2,6-lutidine, which caused to the appearance of a red color. The solution was heated in a sealed ampoule for 18 h at 75°. After extraction of the product in the usual manner, and evaporation of the solvent, the IR spectrum of the residue indicated that almost all the sulphone isomerized to its γ-methylpropargyl isomer.

Kinetic Measurements. The same general procedure,[28,19] described below was employed for the determination of the kinetic data of both propargylic esters presented in Table 2. Appropriate quantities of the ester and base were weighed in a volumetric flask, and the appropriate solvent was added to the mark. Portions of this solution were transfered to ampoules containing a volume of slightly over 5 ml. After the ampoules were sealed and immersed in a constant temperature bath, they were removed at different time intervals and quenched in ice-water. A 5 ml aliquot was removed from the ampoule and transfered to a 50 ml separatory funnel containing 25 ml of ether. After washing with two 10 ml portions of 1N HCl and with three 10 ml portions of water, drying over anhydrous potassium carbonate, and subsequent evaporation of the ether at the water aspirator, the residue was diluted with 1·0 ml of chloroform. This solution was transfered to a 0·1 mm sodium chloride cell, previously balanced with a reference cell, and the infrared spectrum recorded on a model IR 5 Beckman infrared spectrophotometer. The region of 10–13 μ was scanned at room temperature to determine the absorbance of the sulphinate esters. The peak at 857 cm^{-1} for the α,α-dimethylpropargyl ester and the peak at 900 cm^{-1} (CCl_4) for the α-metylpropargyl ester, were used. The value of log (I_0/I) was measured by the base line technique. Before using this method, a control run was preformed to ensure that a linear relationship between absorbance and concentration was obeyed after the extraction procedure has been carried out. The rate constants presented in Table 2 were calculated from the first order kinetic expression, $k = (2{\cdot}303/t) \log (A_0/A)_{obs.}$

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