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# REACTION OF ARYLMETHANESULFONYL AND STYRYLMETHANESULFONYL CHLORIDES WITH TRIETHYLAMINE

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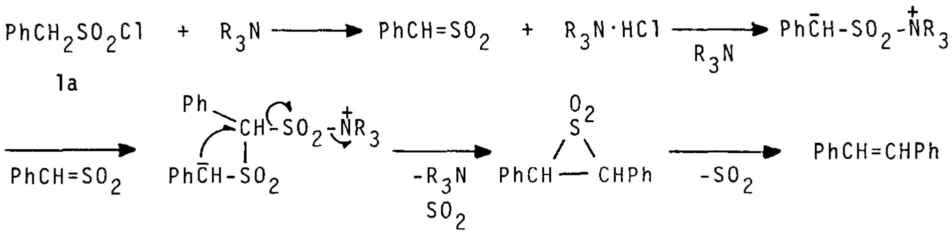
Summary: A series of arylmethanesulfonyl chlorides were treated with triethylamine in THF to give stilbenes in excellent yields. Workup of the mixtures below 10 °C permits isolation of stilbene episulfones which on warming decompose to yield the corresponding stilbenes stereospecifically. Application of the reaction to 9-fluorenylsulfonyl chloride affords bifluorenylidene, while trans-styrylmethanesulfonyl chloride gives 4,5-dihydro-4,5-diphenylthiepin 1,1-dioxide and 1,6-diphenylhexatriene.

Although a variety of sulfenes can currently be generated from diverse precursors and their chemisty is a matter of extensive works,[1] only two examples that sulfene intermediates form olefins as final products are known. One is the formation of stilbenes by treatment of phenylmethanesulfonyl chloride (1a) with bases, and the other is the formation of olefins by reactions of sulfenes with diazoalkanes.[2] In 1911 Wedekind and Schenk proposed the name "sulfene" for $R_2C=SO_2$ and made the first planned attempt to prepare phenyl sulfene by treatment of 1a with $Et_3N$, which led to the isolation of trans-stilbene.[3] About fifty years later, King and Durst who investigated this reaction in detail from a mechanistic point of view found that the reaction in polar solvents yields cis-stilbene episulfone (3a) (which on warming decomposes to give cis-stilbene) in addition to trans-stilbene,[4,5] and proposed the mechanism depicted below on the available experimental data.[6] To the best of our knowledge, the generality and synthetic utility of this reaction has not been well established. The purpose of the present work is to clarify the scope and limitation of this historically important and unique olefin-forming reaction and to know more about its usefulness in organic synthesis.



Arylmethanesulfonyl chlorides (1) were conveniently prepared as follows. Arylmethyl chlorides were stirred with aqueous sodium sulfite at 100 °C for several hours in a two phase mixture using trioctylmethylammonium chloride as the phase transfer agent.

The resulting sodium arylmethanesulfonates were chlorinated by phosphorus pentachloride moistened with phosphorus oxychloride at 0 °C and then warming to room temperature. All of **1** thus obtained are thermally labile except **1a** and evolve sulfur dioxide at their melting points (below 100 °C).[7]

$$ArCH_2Cl \xrightarrow[(C_8H_{17})_3MeN^+Cl^-]{Na_2SO_3} ArCH_2SO_3Na \xrightarrow{PCl_5\text{-}POCl_3} \underset{\mathbf{1}}{ArCH_2SO_2Cl}$$

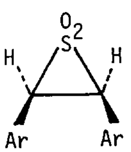
The following procedure was found to give the optimum yield of stilbenes from **1a**. To a stirred solution of **1a** in THF was added excess $Et_3N$ (3 mol. equiv.) at -50 °C, and after 1 h the mixture was warmed to room temperature and stirred overnight. Chromatographic workup of the mixture gave cis- and trans-stilbenes in 93% yield in a ratio of 29:71. In a similar way a series of **1** were treated with $Et_3N$. Results are summarized in Table.
The Table shows that the reaction is quite general yielding the corresponding stilbenes (**2**) in excellent yields. The only side reaction observed is the formation of p-tolualdehyde in run 3.[8] Usually **2** are formed as mixtures of cis- and trans-isomers in a ratio of about 1:2 except runs 5 and 7 where the trans-isomers were exclusively formed.

Table Preparation of Stilbenes from Arylmethanesulfonyl Chlorides: $\underset{\mathbf{1}}{Ar\text{-}CH_2\text{-}SO_2Cl} \xrightarrow[THF]{Et_3N} \underset{\mathbf{2}}{Ar\text{-}CH{=}CH\text{-}Ar}$

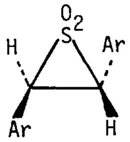
| run | Ar | yield of stilbenes (%) | cis:trans | run | Ar | yield of stilbenes (%) | cis:trans |
|---|---|---|---|---|---|---|---|
| 1 | $C_6H_5$ | 93 | 29:71 | 5 | $2\text{-}ClC_6H_4$ | 88 | 100 |
| 2 | $3\text{-}MeC_6H_4$ | 95 | 33:67 | 6 | $4\text{-}ClC_6H_4$ | 92 | 29:71 |
| 3 | $4\text{-}MeC_6H_4$ | 79[a] | 37:63 | 7 | $2,4\text{-}Cl_2C_6H_3$ | 89 | 100 |
| 4 | $2,5\text{-}Me_2C_6H_3$ | 89 | 32:68 | | | | |

[a] The formation of p-tolualdehyde as byproduct was observed.

Effort was next made to isolate stilbene episulfones in order to know whether they generally exist as precursor compounds of stilbenes. When the reaction of **1a** with $Et_3N$ in THF was quenched below 10 °C by adding ice-water and the resulting precipitate was collected and washed with cold $CCl_4$ to remove trans-stilbene, cis-stilbene episulfone **3a**[4] could be satisfactorily isolated. Similarly the reaction of p-tolylmethanesulfonyl chloride with $Et_3N$ permitted the isolation of the episulfone which on warming decompose to give cis-4,4'-dimethylstilbene. It is therefore assigned as cis-4,4'-dimethylstilbene episulfone (**3b**)[9] in the light of the fact that the formation of olefins by extrusion of sulfur dioxide from episulfones occurs stereospecifically with retention of the original stereochemistry.[10,11] The episulfone (**3c**)[9] was also obtained from p-chloromethanesulfonyl chloride. In the above



3a: Ar = $C_6H_5$
3b: Ar = $4\text{-}MeC_6H_4$
3c: Ar = $4\text{-}ClC_6H_4$

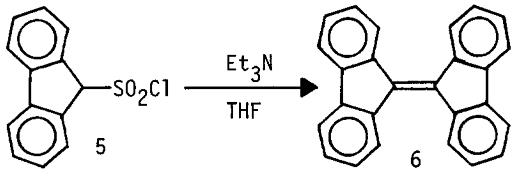


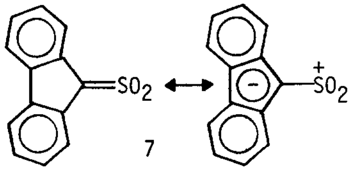
4a: Ar = $2\text{-}ClC_6H_4$
4b: Ar = $2,4\text{-}Cl_2C_6H_3$

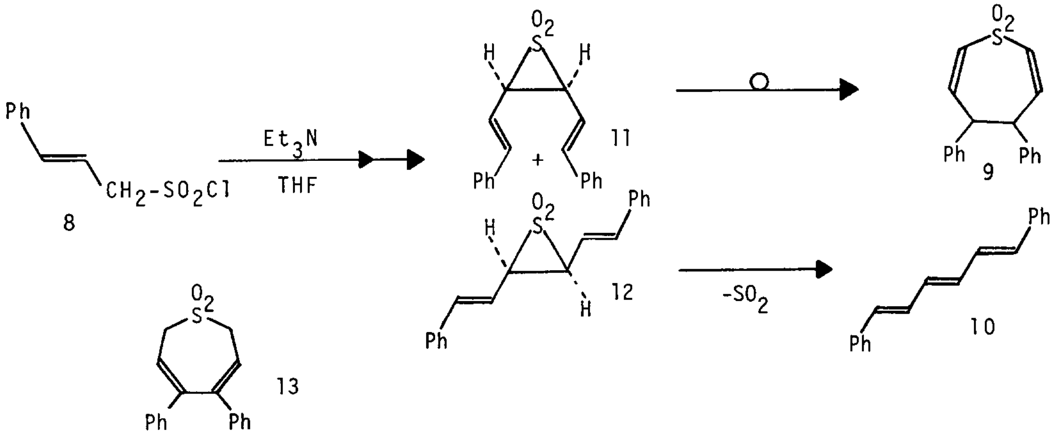
cases, no trans-isomers could be isolated probably because they are thermally labile and decompose under the conditions to give trans-stilbenes. Interestingly enough, however, the reactions of o-chloro- and 2,4-dichlorophenylmethanesulfonyl chlorides with $Et_3N$ cleanly afforded episulfones which on warming gave rise to trans-2,2'-dichloro- and trans-2,2',4,4'-tetrachlorostilbenes and are accordingly identified as trans-2,2'-dichloro- and trans-2,2',4,4'-tetrachlorostilbene episulfones (4a and 4b),[9] respectively. This can account for the exclusive formation of the trans-stilbenes in runs 5 and 7.[12]

Since it has now been well demonstrated that a series of 1 react with $Et_3N$ in THF to give excellent yields of the corresponding stilbenes via stilbene episulfones, application of the reaction to more special cases was next examined. Paquette et al. reported that attempts to prepare stable solutions of electronically stabilized sulfene (7) by treatment of 9-fluorenylsulfonyl chloride (5) with $Et_3N$ in ether is without success and careful evaporation of the solvent leaves a bright yellow solid which is polymeric.[13] We now found that treatment of 5 with $Et_3N$ in THF, to our surprise, gives bifluorenylidene (6) in 40% yield.

Of particular interest is the reaction of trans-styrylmethanesulfonyl chloride (8)[14] with $Et_3N$ in THF which afforded 4,5-dihydro-4,5-diphenylthiepin 1,1-dioxide (9) in 32% yield in addition to the expected hexatriene (10, 6%). The structure proof of 9 is based on spectroscopic data[15] and its quantitative isomerization to the known sulfone (13)[16] induced by t-BuOK in benzene. The most probable explanation of the results involves a Cope type rearrangement of the cis-episulfone intermediate (11) yielding 9 and sulfur extrusion of the trans-isomer (12) giving 10. The Cope type rearrangement of divinyl episulfones is not unprecedented.[17]







Finally a simple alkanesulfonyl chloride was treated with $Et_3N$ in THF. No expected

8-hexadecene was obtained from octanesulfonyl chloride. We therefore conclude that the olefin-forming reaction, i.e., the formation of episulfones is characteristic of arylmethanesulfonyl chlorides and probably of vinylmethanesulfonyl chlorides.

## References and Notes

1. For a recent review on sulfene, see J. F. King, *Acc. Chem. Res.*, **8**, 10 (1975).
2. For a review on this topic, see N. H. Fischer, *Synthesis*, 393 (1970). See also T. Aoyama, S. Toyama, N. Tamaki, and T. Shioiri, *Chem. Pharm. Bull.*, **31**, 2957 (1983).
3. E. Wedekind and D. Schenk, *Ber.*, **44**, 198 (1911).
4. J. F. King and T. Durst, (a) *Tetrahedron Lett.*, 585 (1963), (b) *J. Am. Chem. Soc.*, **85**, 2676 (1963), and (c) *Canad. J. Chem.*, **44**, 819 (1965).
5. Treatment of **1a** with $Et_3N$ in a less polar solvent, cyclohexane, yields a mixture of cis- and trans-oxythiobenzoyl chlorides.[4]
6. J. F. King and D. R. K. Harding, *Canad. J. Chem.*, **54**, 2652 (1976).
7. The following **1** are new compounds. Ar = 3-$MeC_6H_4$, mp 49.5-50.5 °C. Ar = 2,5-$Me_2C_6H_3$, mp 90-90.5 °C.
8. *p*-Tolualdehyde may arise from the reaction of *p*-tolyl sulfene with $SO_2$. For reaction of $PhCH{=}SO_2$ with $SO_2$ yielding benzaldehyde, see J. F. King and M. Aslam, *Canad. J. Chem.*, **57**, 3278 (1979).
9. The chemical shifts of the three-membered ring protons ($CDCl_3$ as solvent) and $\nu SO_2$ (KBr disk) of new episulfones are as follows. **3b**: $\delta$ 4.77; $\nu SO_2$ 1320 and 1140 $cm^{-1}$. **3c**: $\delta$ 4.82; $\nu SO_2$ 1320 and 1145 $cm^{-1}$. **4a**: $\delta$ 4.90; $\nu SO_2$ 1320 and 1180 $cm^{-1}$. **4b**: $\delta$ 4.70; $\nu SO_2$ 1320 and 1170 $cm^{-1}$.
10. F. G. Bordwell, J. M. Williams, Jr., E. B. Hoyt, Jr., and R. B. Jarvis, *J. Am. Chem. Soc.*, **90**, 429 (1968).
11. E. Block, "Reactions of Organosulfur Compounds," Academic Press, New York, 1978, p. 270.
12. The reason why the trans-isomers are exclusively formed in these cases remains as an open question. One of plausible explanations involves $Et_3N$-induced isomerization of the cis-episulfones to the trans-isomers. For methoxide-induced isomerization of cis-stilbene episulfone to the trans-isomer, see ref. 10.
13. L. A. Paquette, J. P. Freeman, and R. W. Houser, *J. Org. Chem.*, **34**, 2901 (1969).
14. Compound **8**, mp 48.5-49.0 °C (dec.), which is thermally labile and decomposes yielding trans-cinnamyl chloride, was prepared in a similar procedure as described with **1**.
15. Compound **9**, mp 170-170.5 °C (dec.). $^1H$-NMR ($CDCl_3$) $\delta$ 4.64 (2H, d, J = 6 Hz, methine), 6.43 (2H, d/d, J = 10 and 6 Hz, olefinic), 6.7-6.9 (6H, m, olefinic + aromatic), and 7.1-7.4 (6H, m, aromatic). IR (KBr disk) $\nu SO_2$ 1290 and 1130 $cm^{-1}$. MS m/e 296 ($M^+$) and 232 ($M^+$-$SO_2$). The cis-trans stereochemistry of this compound was not determined, though the compound seems geometrically pure.
16. The sulfone **13** obtained by isomerization of **9** melted at 190 °C (lit., mp 190 °C); R. M. Dodson and J. P. Nelson, *J. Chem. Soc., Chem. Commun.*, 1159 (1969).
17. W. L. Mock, *J. Chem. Soc., Chem. Commun.*, 1254 (1970); L. A. Paquette and S. Maiorana, *J. Chem. Soc., Chem. Commun.*, 313 (1971).

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