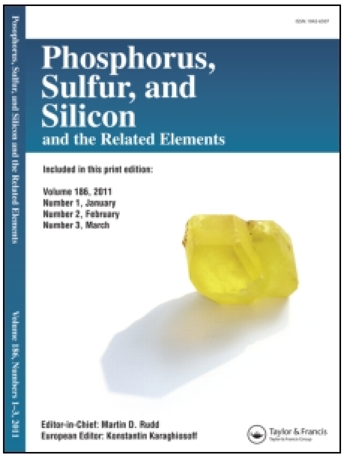

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SYNTHESIS AND SPECTRAL STUDIES OF 2-(ARYLCYCLOPROPYL)STYRYL SULPHONES AND BIS[2-(ARYLCYCLOPROPYL)]SULPHONES

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SYNTHESIS AND SPECTRAL STUDIES OF 2-(ARYLCYCLOPROPYL)STYRYL SULPHONES AND BIS[2-(ARYLCYCLOPROPYL)]SULPHONES†

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Bis(styryl)sulphones on reaction with one or two moles of dimethylsulphonium methylide in the presence of one or two moles of potassium *t*-butoxide yielded 2-(arylcyclopropyl)styryl sulphones and bis[2-(arylcyclopropyl)]sulphones respectively. The compounds are characterised and confirmed to be *trans* isomers by IR and PMR spectroscopy and the usual analytical methods.

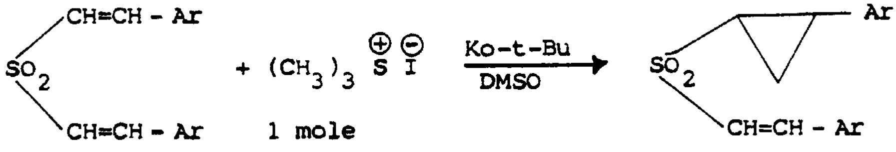
INTRODUCTION

In recent times the use of sulphur ylides as synthetic intermediates has become very important. Among these ylides dimethylsulphonium methylide[1] and dimethylsulphoxonium methylide[1] have been quite extensively studied for their reactions with aldehydes,[2,3] ketones,[4] α,β-unsaturated ketones,[5,6] nitriles,[7] isonitriles[8] and nitro[9] compounds. The reaction of dimethylsulphonium methylide with α,β-unsaturated sulphones for the synthesis of cyclopropyl sulphones[10–12] seemed to be stereoselective. The cyclopropane derivatives thus obtained appeared to have *trans* configuration. Bis-Michael systems were reported to undergo mono[13] or bis[14,15] cyclopropanation with oxosulphonium methylide depending on the ratio of the ylide to the substrate. It was considered to be of interest to examine whether bis(styryl) sulphones upon reaction with the sulphur ylides would lead to the formation of monocyclopropyl and biscyclopropyl sulphones depending upon the amount of ylide used. This type of reactions with compounds containing sulphur have not been reported so far in the literature.

RESULTS AND DISCUSSION

Bis(styryl)sulphones[16] were reacted with one mole of trimethylsulphonium iodide in dimethyl sulphoxide in the presence of one mole of potassium *t*-butoxide yielding 2-(arylcyclopropyl)styryl sulphones **A(1–12)**.

[†] Accepted for presentation at the 4th International Conference on Organic Synthesis held at Tokyo, Japan in 1982.

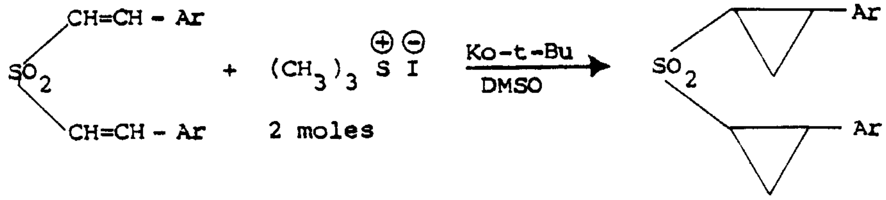


A

where Ar =

A1	4-$CH_3C_6H_4$	**A7**	4-BrC_6H_4
A2	2-FC_6H_4	**A8**	4-$CH_3OC_6H_4$
A3	2-ClC_6H_4	**A9**	2-$C_2H_5OC_6H_4$
A4	3-ClC_6H_4	**A10**	2,5-$(CH_3O)_2C_6H_3$
A5	4-ClC_6H_4	**A11**	3,4,5-$(CH_3O)_3C_6H_2$
A6	2,4-$Cl_2C_6H_3$	**A12**	1-Naphthyl

Similarly a series of bis[2-(arylcyclopropyl)]sulphones **B(1–11)** were also prepared by treating bis(styryl)sulphones with two moles of trimethylsulphonium iodide and potassium *t*-butoxide under identical experimental conditions.



B

where Ar =

B1	4-$CH_3C_6H_4$	**B7**	2,3-$(CH_3O)_2C_6H_3$
B2	2-FC_6H_4	**B8**	2,5-$(CH_3O)_2C_6H_3$
B3	4-FC_6H_4	**B9**	3,4-$(CH_3O)_2C_6H_3$
B4	2-ClC_6H_4	**B10**	3,4,5-$(CH_3O)_3C_6H_2$
B5	4-ClC_6H_4	**B11**	3,4-(—O—CH_2—O—)C_6H_3
B6	2,4-$Cl_2C_6H_3$		

In the infrared spectra of the cyclopropanes, methylene group would give rise to two high frequency bands in the regions 3100–3070 cm^{-1},[17] 3050–3030 cm^{-1}[18] and these bands were used to distinguish the cyclopropane methylene groups from other CH_2 bands of alkanes. The IR spectra of most of the compounds under the present study showed a high frequency band in the region 3060–3030 cm^{-1} (ν_{CH_2} asymmetric) and five compounds showed a band in the region 3120–3080 cm^{-1} (ν_{CH_2} symmetric). These compounds also displayed bands in the region 1050–1010 cm^{-1} (see Table I) which were considered to be the most characteristic of the cyclopropane deformation

TABLE I

Characteristic IR bands exhibited by 2-(Arylcyclopropyl)styryl sulphones **A(1–12)** and bis[2-(arylcyclopropyl)]sulphones **B(1–11)**

Compound number	ν_{CH_2} (cm^{-1}) 3100–3070 region	ν_{CH_2} (cm^{-1}) 3033–2955 region	Ring deformation (cm^{-1}) 1026 region	δ_{CH_2} (cm^{-1}) 866 region	ν_{SO_2} (cm^{-1}) 1300 region	ν_{SO_2} (cm^{-1}) 1150 region	Absorption bands at cm^{-1} 1110 region	Absorption bands at cm^{-1} 910 region	$\nu_{C=C}$ 1620 (cm^{-1}) region	δ_{CH} out-of plane 970 cm^{-1} region
A1	—	3040	1020	870	1300	1130	1070	910	1615	975
A2*	—	3040	1020	855	1290	1110	1080	—	1610	950
A3	—	3030	1030	865	1305	1125	1080	910	1615	970
A4	—	—	1050	865	1305	1120	1050	910	—	970
A5	3120	3060	1010	870	1300	1130	1090	910	1620	970
A6	—	3040	1050	860	1300	1125	1105	—	1615	970
A7	3110	3050	1015	875	1300	1135	1095	915	1630	975
A8	3100	3050	1020	865	1290	1130	1110	910	1610	970
A9	3080	3050	1040	880	1300	1120	1065	910	—	970
A10*	—	—	1035	855	1295	1120	1080	920	1610	970
A11	—	—	1020	850	1300	1120	—	910	1605	970
A12*	—	3050	1025	880	1300	1120	1080	908	1610	965
B1*	—	—	1020	880	1305	1120	1095	915	—	—
B2*	—	3050	1030	860	1295	1125	1090	908	—	—
B3*	—	3040	1040	860	1295	1120	1095	908	—	—
B4*	—	3050	1025	850	1290	1120	1080	908	—	—
B5	3085	3040	1035	865	1300	1130	1090	915	—	—
B6	3120	3060	1015	860	1305	1115	1090	925	—	—
B7*	—	—	1040	865	1300	1130	1070	935	—	—
B8*	—	—	1030	870	1305	1120	1095	930	—	—
B9	—	3040	1030	855	1305	1130	1105	930	—	—
B10*	—	3060	1040	850	1300	1130	1070	935	—	—
B11	—	3060	1035	875	1290	1120	1095	920	—	—

*The infrared spectra were recorded as Nujol mulls and all other compounds as KBr pellets.

mode of the ring.[17,18-20] All the cyclopropyl sulphones under the present study exhibited medium to weak bands in the region 880–850 cm^{-1}, which in addition to the 1050–1010 cm^{-1} bands confirm the presence of cyclopropane ring system.[21,22] Most of the 2-(arylcyclopropyl)styryl sulphones **A(1–12)** exhibited bands in the region 1620–1605 cm^{-1} and 975–950 cm^{-1} in which the former bands are characteristic of C=C bands present in these molecules[23] and the latter bands confirm the *trans* configuration of the styryl moiety present in these molecules.[24] All these compounds (**A** and **B**) exhibited bands with varying intensities at 1110–1050 and 935–908 cm^{-1} confirming the *trans* configuration of cyclopropanes.[10] These compounds have also exhibited very strong peaks characteristic of sulphonyl groups[25,26] in the regions 1305–1290 and 1135–1110 cm^{-1}.

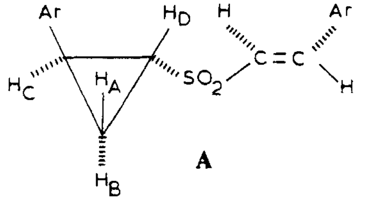
It has been observed that hydrogen attached to cyclopropane ring shows proton magnetic resonance in the region 1.0–2.0 ppm[27] and the appearance of a signal here is considered to be a strong indication of the presence of a cyclopropane ring.[28] The PMR spectra of all these 2-(arylcyclopropyl)styryl sulphones **A(1–12)** and bis[2-(arylcyclopropyl)]sulphones **B(1–11)** (see Table II) exhibited complex multiplets for cyclopropane ring in the regions 1.2–2.2 ppm (for CH_2 group) and 2.4–3.3 ppm (for CH group). The aryl groups showed signals in the regions 6.6–8.0 ppm. Apart from coupling constants[29-33] the chemical shifts data have been also used for the structural problems of cyclopropane derivatives.[34-36] A study of chemical shifts of the ring protons and other substituent groups in cyclopropane has indicated,[37] in

TABLE II

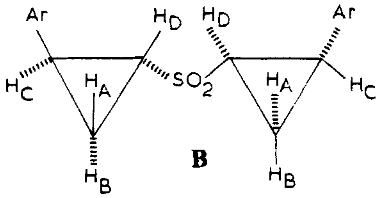
PMR data for 2-(arylcyclopropyl)styryl sulphones **A(1–12)** and bis[2-(arylcyclopropyl)]sulphones **B(1–11)** [Chemical shifts in δ-scale down field from TMS internal standard]

Compound number	Cyclopropyl		Aryl
	CH_2	CH	
A1	1.2–1.9	2.5–2.9	7.0–7.7
A2	1.4–2.2	2.6–3.0	7.0–7.6
A3	1.2–1.9	2.5–3.0	7.0–7.7
A4	1.4–1.9	2.4–3.0	7.2–7.6
A5	1.3–2.1	2.6–3.1	7.3–7.6
A6	1.2–1.9	2.4–3.0	7.2–7.7
A7	1.2–1.9	2.5–2.9	7.2–7.6
A8	1.2–1.9	2.5–2.9	7.2–7.6
A9	1.5–2.0	2.6–3.2	6.7–7.3
A10	1.4–1.9	2.4–3.0	7.2–8.0
A11	1.4–1.9	2.6–3.2	7.0–7.5
B1	1.4–1.9	2.6–3.2	7.0–7.5
B2*	1.5–1.9	2.6–3.2	7.0–7.5
B3	1.3–2.0	2.6–3.0	7.0–7.4
B4	1.5–2.2	2.8–3.3	7.0–7.6
B5	1.4–2.1	2.6–3.1	6.9–7.6
B7*	1.4–1.8	2.7–3.2	6.8–7.1
B8*	1.5–1.9	2.7–3.1	6.7–7.2
B9	1.2–1.9	2.5–2.9	6.6–6.9
B10*	1.5–1.9	2.5–3.1	7.0–7.6

Recorded in * DMSO-d_6 as solvent and all others in $CDCl_3$.



A



B

general, that all substituents tend to cause protons *cis* to them to appear at higher fields than those *trans* to them. In the structures **A** and **B** both H_A and H_B have substituents *cis* to them. Hence H_A and H_B should resonate at higher frequency with a small difference of chemical shifts between them, and this is observed.[38] The chemical shifts for *trans*-1-(phenylsulphonyl)-2-phenyl cyclopropane were reported by Truce and Goralski[38] as complex multiplets in the regions 1.3–2.0 and 2.5–3.0 ppm. The compounds synthesised in the present investigation also showed complex multiplets in the same regions and therefore from this analogy they may be considered as *trans* isomers. The stereoselective procedure adopted for the preparation of these 2-(arylcyclopropyl)styryl sulphones and bis[2-(arylcyclopropyl)]sulphones, IR and PMR spectral data confirm that all these compounds are *trans* (E) isomers.

EXPERIMENTAL

All melting points were determined on a Mel-Temp apparatus and are uncorrected. The elemental analyses were performed by Dr. R. D. MacDonald, Australian Microanalytical Service. The IR spectra were recorded on Beckmann IR-18A as KBr pellets and nujol mulls. The PMR spectra were recorded on a varian XL-100 spectrometer in deuteriochloroform and deuterated dimethyl sulphoxide using TMS as an internal reference.

(E)-Bis(2-chlorostyryl)-, (E)-bis(4-chlorostyryl)-, (E)-bis(4-bromostyryl)-sulphones,[39] (E)-bis(4-methylstyryl)-, (E)-bis(2-fluorostyryl)-, (E)-bis(4-fluorostyryl)-, (E)-bis(3-chlorostyryl)-, (E)-bis(2,4-dichlorostyryl)-, (E)-bis(4-methoxystyryl)-, (E)-bis(2,3-dimethoxystyryl)-, (E)-bis(3,4-dimethoxystyryl)-, (E)-bis(2,5-dimethoxystyryl)-, (E)-bis(3,4,5-trimethoxystyryl)-, (E)-bis[(3,4-methylenedioxy)styryl]-, (E)-bis(2-ethoxystyryl)- and (E)-bis2-[(1-naphthyl)vinyl]-sulphones were prepared as reported earlier.[16] Trimethylsulphonium iodide was prepared according to the procedure of Emeleus and Heal.[40]

General procedure for the preparation of 2-(arylcyclopropyl)styryl sulphones **A(1–12)**. In a 100 ml three neck flask equipped with a magnetic stirrer, a nitrogen inlet tube, a calcium chloride drying tube and a dropping funnel, were placed the bis(styryl)sulphone (0.001 mole), 0.204 g (0.001 mole) of trimethylsulphonium iodide and 20 ml of dry dimethyl sulphoxide. To this well stirred mixture, a solution of 0.112 g (0.001 mole) of potassium *t*-butoxide in 20 ml of dimethylsulphoxide was added dropwise at room temperature (30°C). After the addition was complete, the reaction mixture was stirred for 4 hrs. and then diluted with 500 ml of water. The diluted reaction mixture was stirred overnight or until the cyclopropyl sulphone separated as a solid. The crude cyclopropyl sulphone was filtered, dried and recrystallised from a suitable solvent. Analytical data and other relevant details are presented in Table III.

General procedure for the preparation of bis[2-(arylcyclopropyl)]sulphones **B(1–11)**. By reacting bis(styryl)sulphones with 2 moles of trimethylsulphonium iodide in dimethylsulphoxide in the presence of 2 moles of potassium *t*-butoxide under similar experimental conditions described above for the preparation of **A(1–12)** yielded bis[2-(arylcyclopropyl)]sulphones **B(1–11)**. Analytical data and other relevant details are presented in Table III.

TABLE III

2-(arylcyclopropyl)styryl sulphones **A(1–12)** and bis[2-(arylcyclopropyl)]sulphones **B(1–11)**

				Analysis (%)			
				Calcd.		Found	
Compound number	Yield %	m.p. °C	Formula	C	H	C	H
A1	73	121–123^{a}	$C_{19}H_{20}O_2S$	73.00	6.45	73.08	6.66
A2	75	108–110^{h}	$C_{17}H_{14}F_2O_2S$	63.75	4.37	63.84	4.21
A3	85	124–125^{e}	$C_{17}H_{14}Cl_2O_2S$	57.57	3.99	57.92	4.02
A4	28	223–224^{b}	$C_{17}H_{14}Cl_2O_2S$	57.57	3.99	57.82	4.01
A5	82	132–134^{g}	$C_{17}H_{14}Cl_2O_2S$	57.57	3.99	57.25	3.77
A6	71	153–155^{i}	$C_{17}H_{14}Cl_4O_2S$	48.57	2.85	48.48	2.75
A7	67	142–145^{b}	$C_{17}H_{14}Br_2O_2S$	46.16	3.19	46.17	3.44
A8	63	148–150^{c}	$C_{19}H_{20}O_4S$	66.22	4.85	66.28	5.09
A9	53	136–138^{a}	$C_{21}H_{24}O_4S$	68.39	6.49	68.35	5.95
A10	94	173–175^{f}	$C_{21}H_{24}O_6S$	62.36	5.98	62.13	5.88
A11	72	205–207^{f}	$C_{23}H_{28}O_8S$	59.48	6.03	59.38	6.02
A12	38	146–147^{g}	$C_{25}H_{20}O_2S$	78.12	5.20	78.24	5.10
B1	67	116–118^{c}	$C_{20}H_{22}O_2S$	73.62	6.77	73.61	6.87
B2	90	98–99^{d}	$C_{18}H_{16}F_2O_2S$	64.69	4.79	63.97	5.05
B3	73	128–129^{c}	$C_{18}H_{16}F_2O_2S$	64.69	4.79	64.63	5.03
B4	68	126–127^{e}	$C_{18}H_{16}Cl_2O_2S$	58.86	4.39	58.68	4.64
B5	76	137–138^{c}	$C_{18}H_{16}Cl_2O_2S$	58.86	4.39	59.21	4.64
B6	57	193–195^{b}	$C_{18}H_{14}Cl_4O_2S$	49.77	3.22	49.65	3.38
B7	23	107–109^{d}	$C_{22}H_{26}O_6S$	63.16	6.22	63.14	6.29
B8	76	166–168^{b}	$C_{22}H_{26}O_6S$	63.16	6.22	62.83	5.91
B9	78	160–161^{c}	$C_{22}H_{26}O_6S$	63.16	6.22	62.93	6.19
B10	57	148–149^{c}	$C_{24}H_{30}O_8S$	59.51	6.19	59.84	5.95
B11	77	158–160^{b}	$C_{20}H_{18}O_6S$	62.18	3.70	62.15	3.82

Products recrystallised from (a) aqueous isopropyl alcohol, (b) n-propyl alcohol, (c) methanol, (d) methanol-hexane mixture, (e) aqueous methanol, (f) iso butylalcohol, (g) iso propyl alcohol, (h) aqueous ethanol and (i) aqueous n-propyl alcohol.

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REFERENCES

1. E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 3782 (1962).
2. S. Tanimoto, J. Horikawa and R. Oda, *Yuki Gosei Kagaku Kyokai Shi.*, **27**, 989 (1969); *C.A.* **72**, 32306 g (1970).
3. A. Merz and G. Märkl, *Angew. Chem.*, **85**, 867 (1973).
4. E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **87**, 1353 (1965).
5. B. M. Trost and L. S. Melvin, Jr., *Sulphur Ylides* (Academic Press, New York, 1975), p. 1 and the references cited therein.
6. C. Agami and C. Prevost, *Bull. Soc. Chim. Fr.*, **5**, 2299 (1967).
7. C. Kaiser, B. M. Trost, J. Beeson and J. Weinstock, *J. Org. Chem.*, **30**, 3972 (1965).
8. U. Schoellkopf, R. Harms and D. Hoppe, *Justus Liebigs Ann. Chem.*, 611 (1973).
9. J. Asunskis and H. Schechter, *J. Org. Chem.*, **33**, 1164 (1968).
10. W. E. Truce and C. T. Goralski, *J. Org. Chem.*, **34**, 3324 (1969).
11. C. T. Goralski, *J. Org. Chem.*, **37**, 2355 (1972).
12. M. S. R. Naidu and D. Bhaskar Reddy, *Ind. J. Chem.*, **21B**, 1092 (1982).
13. R. E. Harmon, R. Suder and S. K. Gupta, *Chem. Commun.*, 472 (1972).

14. J. P. Davreux and A. Bruylants, *Bull. Cl. Sci. Acad. Roy. Belg.*, **54**, 823 (1968).
15. Y. Sugimura, N. Soma and Y. Kishida, *Tetrahedron Lett.*, 91 (1971).
16. M. S. R. Naidu and R. Meera Rani, *Proc. Ind. Acad. of Sciences* (in press).
17. S. E. Wiberley and S. C. Bunce, *Anal. Chem.*, **24**, 623 (1952).
18. H. Weitkamp, U. Hasserodt and F. Korte, *Chem. Ber.*, **95**, 2280 (1962).
19. J. Am. Derfer, E. E. Picket and C. E. Boord, *J. Am. Chem. Soc.*, **71**, 2482 (1949).
20. C. F. Wilcox Jr., and R. R. Craig, *J. Am. Chem. Soc.*, **83**, 3866 (1961).
21. J. D. Bartles, R. E. Burk and H. P. Lankelma, *J. Am. Chem. Soc.*, **68**, 2513 (1946).
22. L. J. Bellamy, *Infrared Spectra of Complex Molecules* (John Wiley and Sons Inc., New York, 1960) p. 29.
23. N. B. Colthup, L. H. Daly and S. E. Wiberley, *Introduction to Infrared and Raman Spectroscopy* (Academic Press, New York, 1964) pp. 210–215.
24. W. E. Truce and M. M. Boudakian, *J. Am. Chem. Soc.*, **78**, 2748 (1956).
25. D. Barnard, J. M. Fabian and H. B. Koch, *J. Chem. Soc.*, 2442 (1949).
26. P. M. G. Bavin, G. W. Gray and A. Stephenson, *Spectrochim Acta.*, **16**, 1312 (1960).
27. K. B. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, **83**, 1226 (1961).
28. J. A. Pople, W. G. Schneider and H. J. Bernstein, *High Resolution Nuclear Magnetic Resonance* (McGraw-Hill Book Company, Inc., New York, 1959) p. 237.
29. D. Seyferth, J. M. Burlitch and J. K. Heeren, *J. Org. Chem.*, **27**, 1491 (1962).
30. G. L. Glose, R. A. Moss and J. J. Coyle, *J. Am. Chem. Soc.*, **84**, 4985 (1962).
31. W. E. Truce and V. V. Badiger, *J. Org. Chem.*, **29**, 3277 (1964).
32. D. J. Patel, M. E. H. Howden and J. D. Roberts, *J. Am. Chem. Soc.*, **85**, 3218 (1963).
33. J. D. Graham and M. T. Rogers, *J. Am. Chem. Soc.*, **84**, 2249 (1962).
34. A. Pavia, J. Wylde, R. Wylde and E. Arnal, *Bull. Soc. Chim. Fr.*, 2709, 2718 (1965).
35. L. Vo-Quang and M. P. Simmonin, *Bull. Soc. Chim. Fr.*, 1534 (1965).
36. J. Seyden-Penne and T. Strazalko, *Compt. Rend.*, **260**, 5059 (1965).
37. K. L. Williamson, C. A. Landford and C. R. Nicholson, *J. Am. Chem. Soc.*, **86**, 762 (1964).
38. W. E. Truce and C. T. Goralski, *J. Org. Chem.*, **33**, 3849 (1968).
39. V. Baliah and S. Ananthapadmanabhan, *Indian J. Chem.*, **9(10)**, 1167 (1971).
40. H. J. Emeleus and H. G. Heal, *J. Chem. Soc.*, 1126 (1946).