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STEREOSPECIFIC SYNTHESIS OF SOME NEW Z- AND E-CYCLOPROPYL BENZYL SULFONES AND E,Z- AND E,E-BIS(CYCLOPROPYL)SULFONES BY PTC METHOD

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The title compounds, Z- and E-(2-aryl-3-arylsulfonylcyclopropyl)benzyl sulfones (V & VI) and E,Z- and E,E-bis(2-aryl-3-arylsulfonylcyclopropyl) sulfones (XI & XII) have been prepared by the reaction of aryl thiocarbenes with Z- and E-styryl benzyl sulfones (I & II) and E,Z- and E,E-bis(styryl) sulfones (VII & VIII) under phase transfer conditions. The geometry of the substrates was found to be retained in the product formation as is evidenced by the PMR spectra, thus, confirming the stereospecificity of the reaction. The bioactive nature of the newly synthesized compounds was assayed.

Key words: Z- and E-styryl benzyl sulfones, E,Z- and E,E-bis(styryl)sulfones arylthiocarbenes, cyclopropanation, phase transfer conditions, toxicity evaluation, antimicrobial activity.

INTRODUCTION

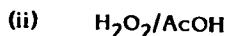
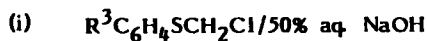
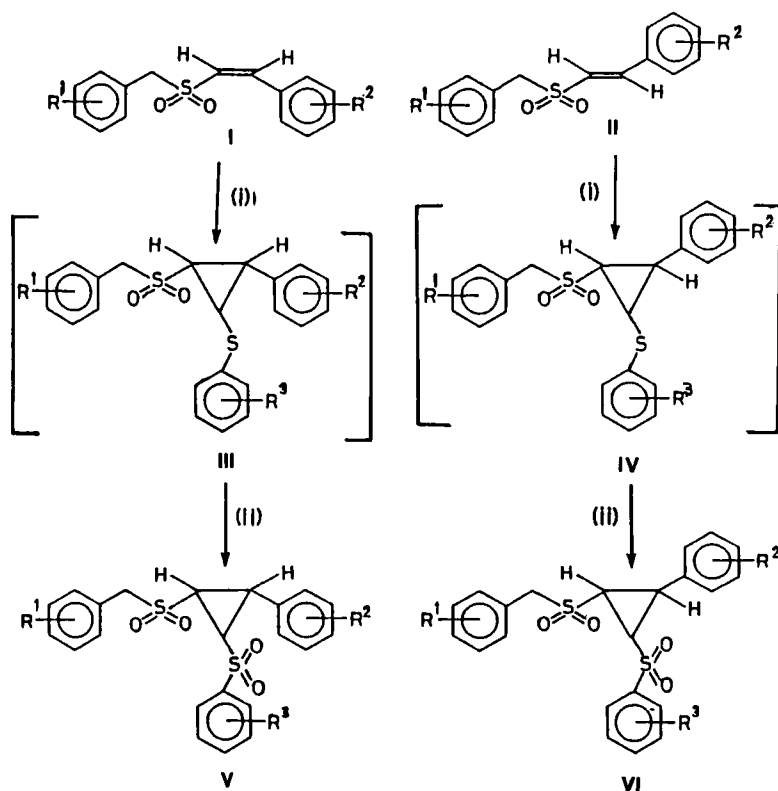
Cycloaddition of carbenes to carbon-carbon double bonds for the preparation of cyclopropane derivatives is a highly general approach. In fact, the chemistry of carbenes and their utility in organic synthesis has been thoroughly reviewed.^{1,2} The majority of carbenes add stereospecifically *cis* to olefinic bonds retaining the geometrical relationship of the substituents. This is evident in the reaction of dibromocarbene with Z- and E-2-butenes.³ In a similar way, several workers have reported the cyclopropanation of olefins with phenoxy and phenylthio carbenes^{4,5} resulting in stereospecifically *cis* compounds. Generation of carbene *in situ* in presence of a strong base usually requires rigorous reaction conditions. On the other hand, with the advent of phase transfer catalysis, the reaction of dihalo or phenylthio carbenes with olefins^{6,7} has become simpler and more versatile. Being interested in the study of addition of carbenes to Michael acceptors,^{8,9} we decided to investigate the addition of arylthiocarbenes to some interesting isomeric mono- and bis(styryl) sulfones.

RESULTS AND DISCUSSION

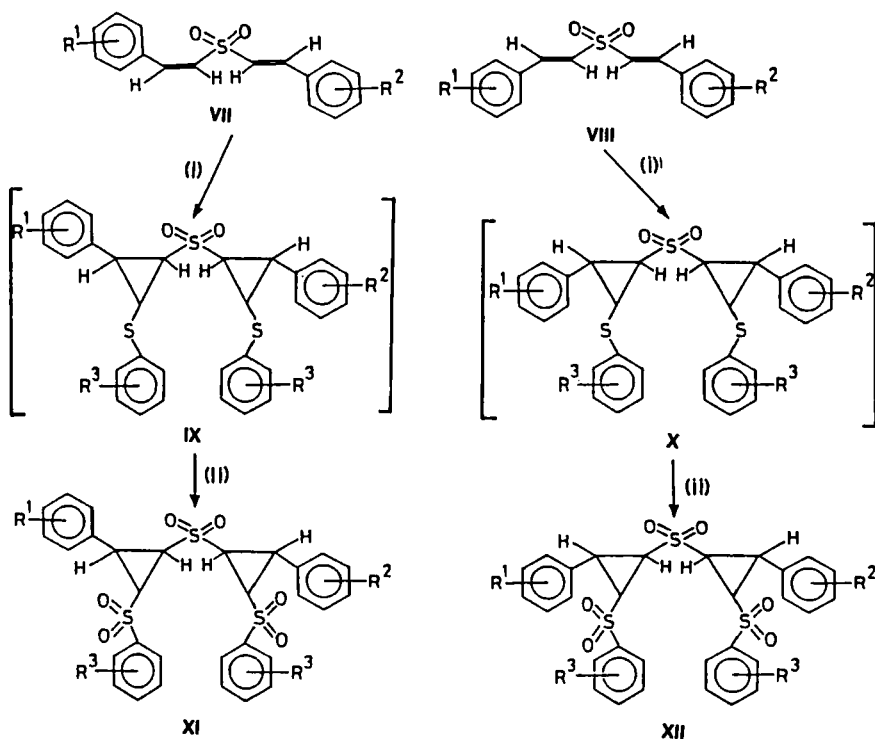
The cycloaddition of arylthiocarbenes to Z- and E-styryl benzyl sulfones (I & II) and E,Z- and E,E-bis(styryl)sulfones (VII & VIII) in the presence of tetrabutylammonium bromide (TBAB) as a phase transfer catalyst led to the formation of Z- and E-(2-aryl-3-aryltiocyclopropyl)benzyl sulfones (III & IV) and E,Z- and E,E-bis(2-aryl-3-aryltiocyclopropyl) sulfones (IX & X). These intermediate thio

compounds were not, however, isolated and the crude products were directly subjected to oxidation with 30% hydrogen peroxide in glacial acetic acid to obtain the target molecules **V**, **VI**, **XI** and **XII** (Schemes I & II and Table I). The *J* values of the cyclopropyl ring protons indicate that the geometry of the substrates **I**, **II**, **VII** and **VIII** have been retained in the products **V**, **VI**, **XI**, and **XII**. Thus, this reaction might have proceeded in a stereospecific manner.^{10,12} On the other hand, when this reaction was carried out in the absence of a phase transfer catalyst under identical conditions, it did not occur. Further, change of catalyst viz., benzyltriethylammonium chloride (BTEAC), cetyltrimethylammonium chloride (CTAC) and dibenzo-18-crown-6 did not improve the yields of the product. Interestingly, the reaction of chloromethylbenzyl sulfides with the substrates **I**, **II**, **VII** and **VIII** in the presence of either BTEAC or TBAB afforded a dimer, $C_6H_5CH_2SCH_2CH_2SCH_2C_6H_5$ instead of a cyclopropyl derivative.

The IR spectra of **V**, **VI**, **XI** and **XII** displayed strong absorption bands in the



SCHEME I



- (i) $R^3C_6H_4SCH_2Cl/50\% \text{ aq. NaOH}$
 $TBAB/CH_2Cl_2$
 (ii) $H_2O_2/AcOH$

SCHEME II

regions $1035\text{--}1015\text{ cm}^{-1}$ due to cyclopropane ring deformations and $1345\text{--}1310$ and $1140\text{--}1120\text{ cm}^{-1}$ for the sulfonyl group.⁹ The structures **Va**, **VIa**, **XIa** and **XIIa** are taken as representative examples to interpret the 1H NMR spectral data. The spectra of all these compounds showed an AMX pattern for the cyclopropyl ring protons and each one of them appeared as doublet of doublets⁹ (Table II). However, in case of **XI** two AMX systems have been observed as a result of the difference in the geometry of the two cyclopropyl ring protons. H_A in all these compounds experiences a stronger deshielding effect than H_M and H_X as a result of adjacent aryl group. Among H_M and H_X , the H_M adjacent to an arylsulfonyl group experiences a similar deshielding influence as in the case of H_A . Perusal of the J values from Table III indicate that the geometry assigned to different protons of the cyclopropane ring is reasonably correct.

The δ_C values of C-1, C-2 and C-3 of the cyclopropyl ring carbons of **V**, **VI**, **XI** and **XII**, obtained from their ^{13}C NMR spectra, are shown in Table IV. The δ_C values of the two cyclopropyl ring carbons of **XI** appeared at different regions for

TABLE I
Melting points and analytical data of V, VI, XI and XII

Compd. No.	R ¹	R ²	R ³	Yield (%)	m.p. (°C)	Mol. formula (mol. wt.)	Found (Calcd.) (%)	
							C	H
Va	H	H	H	71	205-206	C ₂₂ H ₂₀ O ₄ S ₂ (412.52)	63.87 (64.06)	4.77 (4.89)
Vb	H	4-Cl	4-CH ₃	65	215-216	C ₂₃ H ₂₁ ClO ₄ S ₂ (460.99)	60.15 (59.93)	4.71 (4.59)
Vc	4-CH ₃	H	4-Cl	68	225-226	C ₂₃ H ₂₁ ClO ₄ S ₂ (460.99)	59.77 (59.93)	4.51 (4.59)
VIa	4-CH ₃	H	H	75	228-230	C ₂₃ H ₂₂ O ₄ S ₂ (426.35)	64.45 (64.79)	5.10 (5.16)
VIb	4-CH ₃	4-CH ₃	4-Cl	70	242-243	C ₂₄ H ₂₃ ClO ₄ S ₂ (474.81)	60.54 (60.71)	4.76 (4.84)
VIc	4-Cl	4-CH ₃	4-CH ₃	65	218-219	C ₂₄ H ₂₃ ClO ₄ S ₂ (474.81)	60.87 (60.71)	4.96 (4.84)
VId	4-CH ₃	4-Br	4-Cl	78	255-256	C ₂₃ H ₂₀ BrClO ₄ S ₂ (539.88)	51.33 (51.17)	3.80 (3.73)
VIe	4-Cl	4-F	4-CH ₃	68	248-250	C ₂₃ H ₂₀ ClFO ₄ S ₂ (478.98)	57.39 (57.67)	4.12 (4.21)
XIa	H	H	H	68	248-250	C ₃₀ H ₂₆ O ₆ S ₃ (578.70)	62.09 (62.76)	4.48 (4.53)
XIb	H	4-OC ₂ H ₅	4-Cl	72	262-263	C ₃₂ H ₂₈ Cl ₂ O ₇ S ₃ (691.64)	55.31 (55.57)	3.95 (4.08)
XIc	H	4-Cl	4-CH ₃	65	255-256	C ₃₂ H ₂₉ ClO ₆ S ₃ (641.19)	60.15 (59.94)	4.63 (4.56)
XId	4-CH ₃	4-CH-(CH ₃) ₂	H	60	235-236	C ₃₄ H ₃₄ O ₆ S ₃ (634.80)	64.04 (64.33)	5.38 (5.40)
XIe	4-CH ₃	2,4-Cl ₂	4-Cl	70	270-272	C ₃₁ H ₂₄ Cl ₄ O ₆ S ₃ (730.50)	51.17 (50.97)	3.39 (3.31)
XIIa	H	H	H	65	275-276	C ₃₀ H ₂₆ O ₆ S ₃ (578.70)	62.53 (62.26)	4.45 (4.53)
XIIb	H	4-CH ₃	4-Cl	68	282-283	C ₃₁ H ₂₆ Cl ₂ O ₆ S ₃ (661.62)	56.04 (56.27)	4.07 (3.96)
XIIc	H	2,6-Cl ₂	4-CH ₃	64	298-300	C ₃₂ H ₂₈ Cl ₂ O ₆ S ₃ (675.64)	56.72 (56.88)	4.12 (4.18)
XIId	4-CH ₃	2-Cl	H	60	285-286	C ₃₁ H ₂₇ ClO ₆ S ₃ (627.17)	59.52 (59.36)	4.25 (4.34)
XIIe	4-CH ₃	4-CH ₃	4-Cl	72	295-296	C ₃₂ H ₂₈ Cl ₂ O ₆ S ₃ (675.64)	56.59 (56.88)	4.29 (4.18)

similar reasons explained in the PMR spectra. Resonances due to C-3 in these compounds appeared at downfield in comparison to C-1 and C-2 because of the higher deshielding effect exerted by arylsulfonyl group. The ¹³C chemical shift values at 61.32 and 61.40 ppm are attributed to the benzylic carbons in XI and XII, respectively.

Low intensity molecular ion peaks are observed in the 70 eV mass spectra of V

TABLE II
PMR spectral data of V, VI, XI and XII

Compound	Chemical shifts					
	H _A	H _{A'}	H _M	H _{M'}	H _X	H _{X'}
Va	3.90	-	3.50	-	3.35	-
Vc	3.93	-	3.52	-	3.36	-
VIa	3.96	-	3.58	-	3.40	-
VIc	3.92	-	3.55	-	3.38	-
VIe	4.00	-	3.63	-	3.45	-
XIa	4.13	4.03	3.61	3.55	3.45	3.48
XIc	4.15	4.06	3.65	3.58	3.43	3.48
XId	4.10	4.02	3.59	3.52	3.38	3.45
XIe	4.19	4.10	3.68	3.61	3.47	3.55
XIIa	4.18 [†]	-	3.66 ^{††}	-	3.50 ^{†††}	-
XIIb	4.12	4.09	3.60	3.55	3.45	3.40
XIIc	4.19	4.23	3.66	3.72	3.48	3.53
XIIf	4.20 [†]	-	3.69 ^{††}	-	3.52 ^{†††}	-

[†] Value for H_A & H_{A'}; ^{††} value for H_M & H_{M'}; ^{†††} value for H_X & H_{X'}.

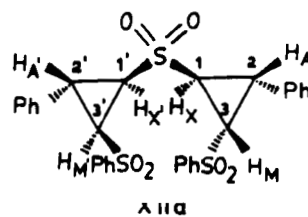
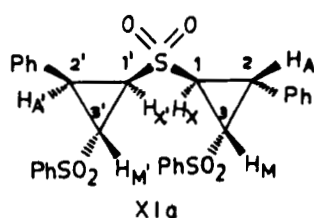
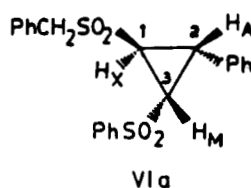
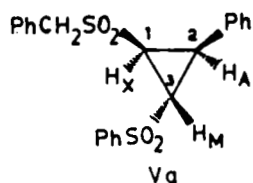


TABLE III
J values of V, VI, XI and XII

Compound	J _(AX)	J _(A'X')	J _(AM)	J _(A'M')	J _(MX)	J _(M'X')
Va	9.88	-	5.02	-	6.42	-
Vc	9.87	-	5.00	-	6.39	-
VIa	6.62	-	9.82	-	4.94	-
VIc	6.65	-	9.84	-	4.96	-
VIe	6.68	-	9.85	-	4.98	-
XIa	6.59	10.01	4.88	6.84	9.76	5.13
XIIa	6.62 [†]	-	4.89 ^{††}	-	9.78 ^{†††}	-
XIIf	6.60 [†]	-	4.86 ^{††}	-	9.77 ^{†††}	-

[†] value for J_(AX) & J_(A'X'); ^{††} value for J_(AM) & J_(A'M'); ^{†††} value for J_(MX) & J_(M'X')

TABLE IV
¹³CMR spectral data of V, VI, XI and XII

Compound	C-1	C-1'	C-2	C-2'	C-3	C-3'
Va	38.78	-	29.25	-	42.82	-
Vc	38.80	-	29.28	-	42.85	-
VIa	39.22	-	29.58	-	43.26	-
VIc	39.18	-	29.52	-	43.19	-
VId	39.48	-	30.73	-	43.85	-
XIa	40.03	39.46	30.25	29.67	44.42	43.85
XIc	40.24	39.59	30.46	29.85	44.60	43.98
XIe	40.29	39.62	30.50	29.92	44.65	44.02
XIIa	40.46 [†]	-	30.85 ^{††}	-	45.03 ^{†††}	-
XIIf	40.52 [†]	-	30.94 ^{††}	-	45.10 ^{†††}	-

[†] value for C-1 & C-1'; ^{††} value for C-2 & C-2';

^{†††} value for C-3 & C-3'

and XI confirming their molecular formulae. A facile elimination of SO₂ or phenylsulfonic acid moiety in a step wise manner, is an unique feature observed in the fragmentation of the molecular ions.⁹ Further α -cleavage processes of the molecular ion is commonly observed in these systems. Tropylium cation (m/z 91) appeared as base peak in the spectrum of Va while phenylcyclopropenium cation (m/z 115) in XI. Interestingly, the cyclopropane ring remains intact during the fragmentation in both the systems. It is also observed that the geometry has no considerable influence on the fragmentation pathway as the mass spectra of V & VI and XI & XII are found to be identical. The different fragmented ions formed in the cleavage of these compounds are shown in Tables V & VI.

TABLE V
 Mass spectral data of Va and VIa

Compd.No/Ions	Va	VIb
M ⁺	412(4)	460(6)
[M-O] ⁺	396(22)	444(15)
[R ¹ R ² R ³ C ₂₂ H ₁₇ OS] ⁺	332(15)	380(22)
[R ¹ R ³ C ₂₂ H ₁₇] ⁺	284(14)	332(10)
[R ² R ³ C ₁₅ H ₁₁ O ₂ S] ⁺	257(25)	305(20)
[R ² R ³ C ₁₅ H ₁₀ O ₂ S] ⁺	256(12)	304(11)
[R ² R ³ C ₁₅ H ₁₁] ⁺	193(32)	241(30)
[R ² R ³ C ₁₅ H ₁₀] ⁺	192(22)	240(25)
[R ² C ₉ H ₆] ⁺	115(27)	129(42)
[R ¹ C ₇ H ₆] ⁺	91(100)	91(100)

TABLE VI
Mass spectral data of **XIa**, **XIc** and **XIle**

Compd. No./Ions	XIa	XIc	XIle
M ⁺	578(3)	-	674(6)
[M-O] ⁺	562(8)	624(7)	658(15)
[M-R ³ C ₆ H ₄ O ₂ S] ⁺	437(16)	485(19)	499(21)
[M-3SO ₂]	386(19)	448(22)	482(16)
[R ¹ R ² R ³ C ₂₄ H ₁₈ O ₂ S] ⁺	373(12)	421(10)	435(12)
[R ¹ R ² C ₁₈ H ₁₃ O ₂ S] ⁺	295(10)	329(8)	323(20)
[R ¹ R ² C ₁₈ H ₁₀ O ₂ S] ⁺	294(12)	328(15)	322(24)
[R ¹ R ³ C ₁₅ H ₁₁ O ₂ S] ⁺	257(49)	271(56)	305(32)
[R ² R ³ C ₁₅ H ₁₁ O ₂ S] ⁺	257(49)	305(28)	305(25)
[R ¹ C ₉ H ₆] ⁺	115(100)	115(100)	129(100)
[R ² C ₉ H ₆] ⁺	115(100)	149(42)	129(100)

Note: Values in the parenthesis indicate the percentage intensity.

'-' indicates absence of a peak.

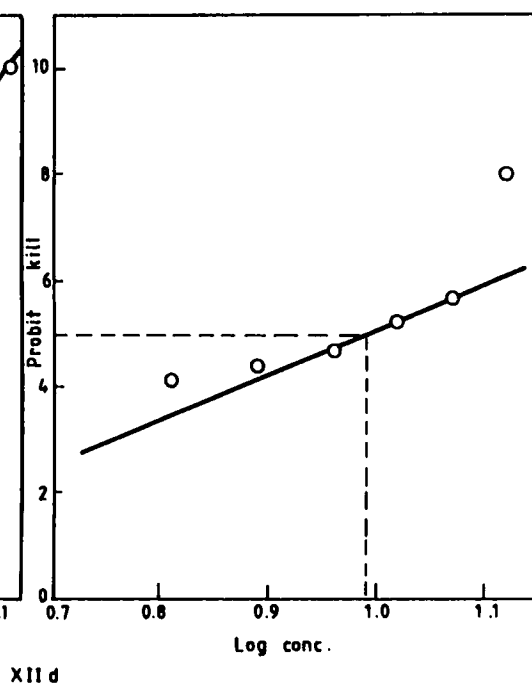
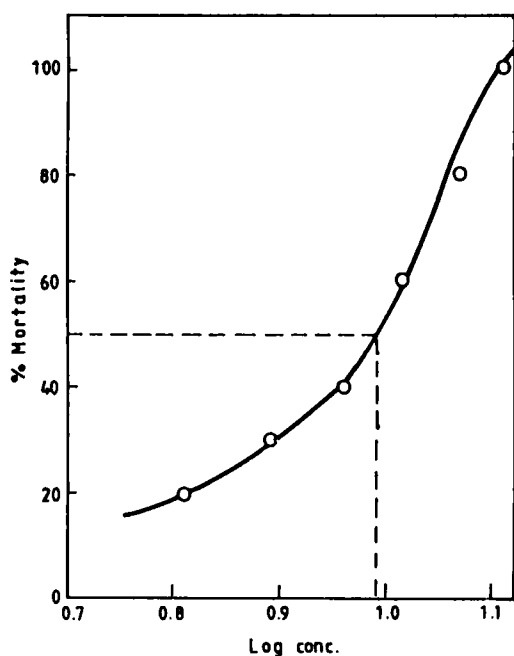
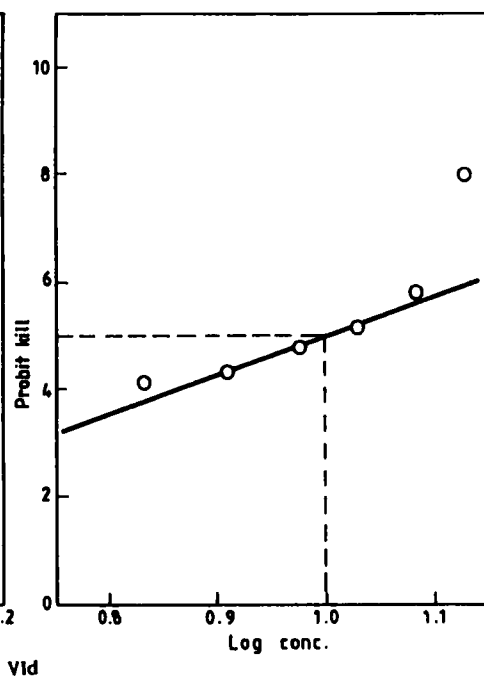
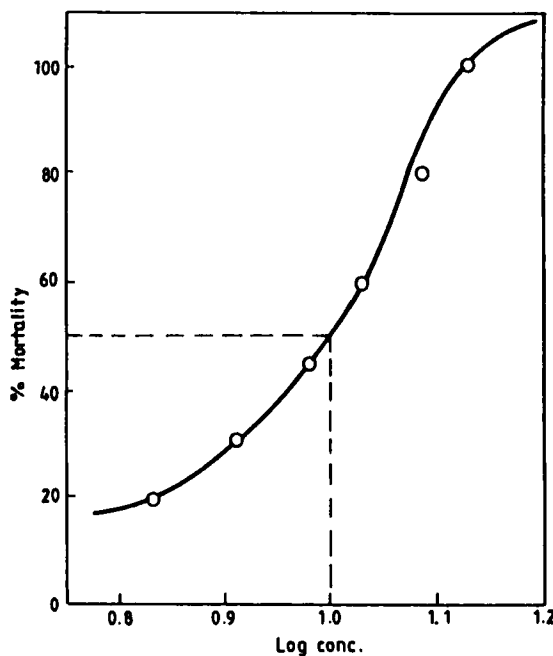
Toxicity evaluation: An attempt has been made to evaluate the toxicity of **V**, **VI**, **XI** and **XII** on the cockroach, *Periplaneta americana*. The LD₅₀ values have been determined by topical application of the compounds to the test species by Finney's probit method.¹⁶ The percentage mortality and probit kill are graphically plotted against the log concentration. The required concentration to kill specific percentages of test species (LD₅₀ mg/kg body wt.) are derived from graphs viz., **Vb** 10.54; **VIa** 10.95; **VId** 9.98; **XIa** 9.76; **XIc** 9.45; **XIIa** 10.38; **XIIc** 9.84. It has been observed that the percentage of mortality increased with increasing concentration of the compounds. Amongst all the compounds, those having halogen substituent in the phenyl moiety showed relatively more toxicity than others and the compound **XIc** exhibited highest activity. Bis(cyclopropyl)sulfones (**XI** & **XII**) displayed higher toxic potential than mono(cyclopropyl)sulfones (**V** & **VI**). Further, a majority of the compounds tested possess LD₅₀ values lower than the standard pesticide fenvalerate (LD₅₀ 12.88 mg/kg body wt.) (Table VII).

Antimicrobial activity: The compounds **V**, **VI**, **XI** and **XII** were evaluated for their antibacterial activity against the organisms, *Staphylococcus aureus*, *Bacillus subtilis* (gram + ve) and *Escherichia coli* (gram - ve) by filter paper disc method.¹⁷ Among them, the compounds **XI** and **XII** showed the greatest activity. The compounds **V**, **VI**, **XI** and **XII** have also been assayed for antifungal activity against the organisms, *Curvularia lunata*, *Fusarium solani* and *Helminthosporium oryzae* by the method described by Horsfall and Rich.¹⁸ All of the compounds tested effectively inhibit spore germination of the three fungi at mg/mL concentration. The results of the investigation reveal that all the compounds possess relatively high inhibiting effect on *F. solani* and *C. lunata* compared to *H. oryzae*. The halogen or methoxy sub-

TABLE VII
The average mortality of *Periplaneta americana* with IX, X, XI and XII

Compd. No.	Conc. of the Compd. mg/kg body wt.	Log conc.	Number of animals		% kill	Probit kill
			Exposed	Dead		
Vb	6.75	0.829	20	3	15	3.96
	8.10	0.908	20	5	25	4.33
	9.45	0.975	20	8	40	4.75
	10.80	1.033	20	12	60	5.25
	12.15	1.084	20	16	80	5.84
	13.50	1.130	20	20	100	8.09
Vla	6.75	0.829	20	3	15	3.96
	8.10	0.908	20	5	25	4.33
	9.45	0.975	20	7	35	4.61
	10.80	1.033	20	9	45	4.87
	12.15	1.084	20	13	60	5.25
	13.50	1.130	20	19	95	6.64
Vld	6.75	0.829	20	4	20	4.16
	8.10	0.908	20	6	30	4.48
	9.45	0.975	20	9	45	4.87
	10.80	1.033	20	12	60	5.25
	12.15	1.084	20	16	80	5.84
	13.50	1.130	20	20	100	8.09
Xla	6.50	0.813	20	4	20	4.16
	7.80	0.892	20	7	35	4.61
	9.10	0.959	20	9	45	4.87
	10.40	1.017	20	12	60	5.25
	11.70	1.068	20	16	80	5.84
	13.00	1.114	20	20	100	8.09
Xle	6.50	0.813	20	5	25	4.33
	7.80	0.892	20	7	35	4.61
	9.10	0.959	20	9	45	4.87
	10.40	1.017	20	13	65	5.39
	11.70	1.068	20	17	85	6.04
	13.00	1.114	20	20	100	8.09
Xlla	6.50	0.813	20	3	15	3.96
	7.80	0.892	20	6	30	4.48
	9.10	0.959	20	8	40	4.75
	10.40	1.017	20	11	55	5.13
	11.70	1.068	20	16	80	5.84
	13.00	1.114	20	20	100	8.09
Xlld	6.50	0.813	20	4	20	4.16
	7.80	0.892	20	6	30	4.48
	9.10	0.959	20	8	40	4.75
	10.40	1.017	20	12	60	5.25
	11.70	1.068	20	16	80	5.84
	13.00	1.114	20	20	100	8.09

stituents in the phenyl moiety enhances the antifungal activity than others. Moreover, compounds **XI** and **XII** displayed greater activity than **V** and **VI** presumably due to the presence of one extra sulfonyl group.



EXPERIMENTAL

Melting points were determined on a Mel-Temp apparatus and are uncorrected. The IR spectra (wave numbers in cm^{-1}) were recorded on a Perkin-Elmer Grating infrared spectrophotometer Model 337 in KBr pellets and on Hitachi Model 270-50 as nujol mulls. The ^1H NMR spectra were recorded in CDCl_3 solution on GE NMR Omega spectrometer operating at 500 MHz and Bruker spectrometer operating at 500 or 200 MHz and ^{13}C NMR spectra at 125 or 50 MHz with TMS as an internal standard. The mass spectra were recorded on Finnigan Mat 1210 B double focussing spectrometer at 70 eV. The microanalyses were performed by Regional Sophisticated Instrumentation Centre, Punjab University, Chandigarh, India.

General procedure for the preparation of Z- and E-(2-aryl-3-arylsulfonylcyclopropyl)benzyl sulfones (V & VI) and E,Z- and E,E-1,1'-bis(2-aryl-3-arylsulfonylcyclopropyl) sulfones (XI & XII)

A mixture of I or II or VII or VIII (References 12–15, 10 mmol), aryl chloromethyl sulfide (for I & II, 10 mmol and for VII & VIII, 20 mmol), in methylene chloride (40 mL) was stirred with 50% aqueous NaOH (20 mL) till a clear two phase system was obtained. A catalytic amount (100 mg) of tetrabutylammonium bromide (TBAB) was then added and the stirring was continued for 4–6 h at room temperature. The progress of the reaction was monitored by TLC. After completion of the reaction, the contents were diluted with water. The organic layer was separated, washed with water and brine and was dried over anhydrous Na_2SO_4 . Evaporation of the solvent gave crude thiocyclopropanes, III, IV, IX and X as viscous liquids which were subsequently oxidized with 30% hydrogen peroxide (10 mL) in glacial acetic acid (20 mL) at reflux temperature for 8–10 h. The contents were allowed to cool and poured onto crushed ice with stirring. The solid products so obtained were collected on a Buchner funnel, washed with water, dried and recrystallized from 2-propanol to obtain pure VI, VII, XI and XII.

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