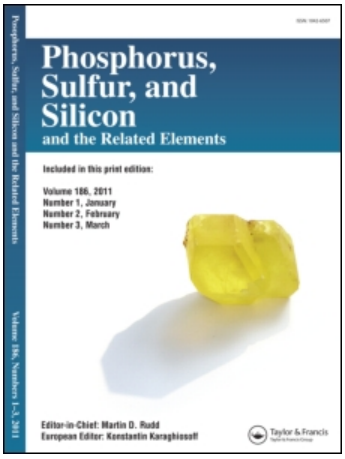

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PHASE TRANSFER CATALYZED CYCLOPROPANATION OF TRANS-STYRYL ARYL SULFONES WITH DIMETHYL SULFOXONIUM METHYLIDE

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PHASE TRANSFER CATALYZED CYCLOPROPANATION OF TRANS-STYRYL ARYL SULFONES WITH DIMETHYL SULFOXONIUM METHYLIDE

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Some new *trans*-aryl cyclopropyl sulfones (**II**) have been prepared by the cycloaddition of dimethylsulfoxonium methylide to *trans*-styryl aryl sulfones (**I**) by two different methods. It is observed that the reaction in presence of a phase transfer catalyst proceeds in a facile manner.

Keywords: *E*-styryl aryl sulfones; trimethylsulfoxonium iodide; cyclopropanation; phase transfer catalysis; antimicrobial activity

INTRODUCTION

Cyclopropanation of olefins constitutes an important carbon-carbon bond forming reaction[1–4]. In recent years the chemistry of cyclopropanoids has drawn the attention of synthetic organic chemists not only due to their pronounced bioactive nature but also due to their function as active intermediates in organic synthesis. Apart from this, compounds having the sulfonyl moiety were also known to be physiologically active[5]. Hence, much attention is now being paid to the synthesis of newer cyclopropanes containing a sulfonyl functionality by a viable and facile method. Among various methods developed over the years for this purpose, cycloaddition of sulfur ylides to activated olefins is an important and elegant synthetic strategy[6]. A number of publications has appeared on the cyclopropanation of sulfonyl activated olefins under homogeneous conditions[7–9]. This

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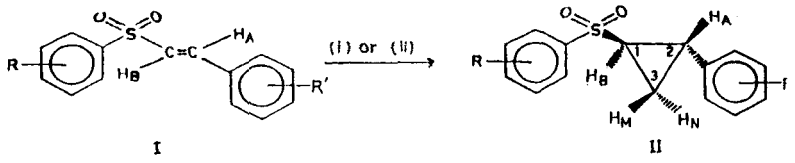
method however, requires rigorous reaction conditions leading to the formation of products in poor yields. The phase transfer catalysis method which is of recent origin has been very much exploited for the cyclopropanation of olefins. In our sustained effort to establish the unprecedented reactivity of the phase transfer catalysis which has become a versatile tool in all the important new reactions led us to plan for the synthesis of cyclopropyl sulfones.

RESULTS AND DISCUSSION

In one method (Method A) the *trans*-styryl aryl sulfones (**I**) were treated with trimethylsulfoxonium iodide in dichloromethane and 50% aq. NaOH in the presence of benzyltriethylammonium chloride (BTEAC), as a phase transfer catalyst to obtain *trans*-1-arylsulfonyl-2-arylcyclopropanes (**II**) (Scheme and Table I). The ylide, dimethylsulfoxonium methylide is presumably generated *in situ* from trimethylsulfoxonium iodide in the reaction medium. In contrast when the same reaction was carried out in the absence of a catalyst cyclopropanation did not occur. On the other hand when this reaction was carried out in the presence of potassium t-butoxide as a base in dry dimethyl sulfoxide at room temperature the reaction did takes place (Method B)[10]. The ylide is generated *in situ* in this case also. The reaction proceeds under phase transfer conditions in a facile and viable manner (Method A, 74–83%) compared to the other method (Method B, 52–68%). Moreover, this technique (PTC) offers improved reaction rates under mild conditions not only for cyclopropanation[11] but also for a variety of reactions[12]. Analysis of ^{1}H NMR spectra of **II** showed that J_{AB} is between 5–6 Hz indicating the *trans*-geometry[13]. Indeed cyclopropanation of a number of *trans* unsaturated esters, amides and sulfones with dimethylsulfonium methylide were reported to yield stereoselectively the corresponding *trans*-cyclopropane derivatives[6, 13–15].

The IR spectra (ν_{max} in cm^{-1}) of **II** showed strong bands in the region 1040–1020 confirming the presence of a cyclopropane ring[16]. Bands with varying intensities have also been displayed by these compounds in the region 1110–1080 and 940–920 (*trans*configuration) 1330–1300 and 1140–1120 (νSO_2). The ^{1}H NMR spectra ($CDCl_3$) of **II** exhibited an ABMN pattern. The methine (H_A, H_B) and methylene (H_M, H_N) protons of cyclopropyl ring due to vicinal and geminal couplings each one of them appeared as a doublet of a double doublet (Table II). The H_A absorbed at



I II

(i) $(CH_3)_3$ S(O) I / 50% aq-NaOH / BTEAC / CH_2Cl_2

(ii) $(CH_3)_3$ S(O) I / t-BuOK / DMSO

SCHEME

downfield region due to the deshielding effect exerted by aryl moiety[14]. Besides this, H_M which is *trans* to phenyl moiety experiences more deshielding effect and appeared at higher δ_H values than H_N. In cyclopropyl systems $J_{cis} > J_{trans}$[17]. The J values for methylene and methine protons of **II** were found to be $J_{AB} = 5.50–5.65$, $J_{AM} = 8.30–8.40$, $J_{AN} = 6.50–6.58$, $J_{BM} = 5.30–5.40$, $J_{BN} = 9.96–10.05$, and $J_{MN} = 4.40–4.50$ H_Z. Thus, the geometry of different protons are H_A $H_B = H_B$ $H_M = H_A H_N$ = *trans*; H_A $H_M = H_B$ H_N = *cis*; H_M H_N = geminal. The δ_C values in Table III indicate that C-3 absorbs at upfield region in comparison to C-1 and C-2 for similar reasons as explained above. The mass spectra of **IIa, IIb, IIc** and **IId** at 70 eV showed low abundant molecular ion peaks at 258, 272, 292 and 337 respectively. α-Cleavage process, facile elimination of SO_2 and ejection of one or two molecules of hydrogen are some of the prominent features observed in the fragmentation of molecular ion[16]. The phenylcyclopropyl cation appeared as base peak of the spectra.

EXPERIMENTAL

All the melting points are uncorrected and were determined on a Mel-Temp apparatus. IR spectra were recorded on a Perkin-Elmer Grating Infrared Spectrophotometer as KBr pellets. The ^1H and ^{13}C NMR spectra were recorded at 500 or 200 MHz and 1250 or 50 MHz respectively on a GE NMR Omega instrument and on a Bruker spectrometer with TMS as an internal standard. The mass spectra were recorded on Finnigan Mat 1210-B mass spectrometer. Microanalyses were performed by Regional Sophisticated Instrumentation Centre, Punjab University, Chandigarh, India.

TABLE I Physical and IR data of II

Compd. No.	*R*	*R'*	*m.p. (°C)*	*Yield (%)*		SO_2	*IR Spectra (cm^{-1})*	
				Method 'A'	*Method 'B'*		*trans vibration*	*ring deformation*
IIa	H	H	94–96	77	63	1315, 1120	1085,925	1020
IIb	H	4-CH_3	101–103	74	60	1310, 1125	1080,925	1020
IIc	H	4-Cl	100–102	78	62	1320, 1125	1100,930	1030
IId	H	4-Br	102–103.5	79	61	1325,1120	1085,935	1030
IIe	H	3,4-$(OCH_3)_2$	94–95	81	-	1320, 1125	1080,930	1025
IIf	4-CH_3	H	137–139	75	55	1315, 1125	1090,920	1020
IIg	4-CH_3	4-CH_3	147–148	83	-	1310, 1120	1085,925	1025
IIh	4-CH_3	4-Cl	125–127	80	-	1320, 1125	1090,925	1030
IIi	4-OCH_3	H	124–125.5	82	-	1315,1120	1085,920	1020
IIj	4-OCH_3	4-OCH_3	108–109	82	-	1320, 1125	1080,925	1020
IIk	4-OCH_3	4-Cl	121–123	78	66	1325,1130	1080,930	1035
III	4-Cl	H	111–112	80	52	1310,1120	1095,930	1030
IIm	4-Cl	4F	100–102	82	-	1320, 1125	1095,920	1040
IIn	4-Cl	3,4-$(OCH_3)_2$	118–120	79	68	1325,1130	1080,930	1030
IIo	4-Br	H	104–106	77	67	1310,1135	1085,925	1025

Compd. No.	*R*	*R'*	*m.p. (°C)*	*Yield (%)*		SO_2	*IR Spectra (cm^{-1})*	
				Method 'A'	*Method 'B'*		*trans vibration*	*ring deformation*
IIp	4-Br	4-OCH_3	130–131.5	78	-	1300, 1120	1080,920	1020
IIq	4-Br	2-Cl	103–104	75	-	1310,1125	1090, 925	1030
IIr	3,4-Cl_2	H	115–117	74	61	1320, 1130	1110,930	1040
IIs	3,4-Cl_2	4-Cl	131–133	76	58	1330, 1140	1080,940	1030
IIt	4-Cl, 3-CH_3	H	99–100.5	80	66	1315, 1125	1085,930	1030
IIu	4-Cl, 3-CH_3	2-Cl	113–115	78	63	1310, 1120	1080,930	1020
IIv	4-Cl,3-CH_3	2-Cl	124–126	75	60	1320, 1135	1085,935	1040
IIw	4-Cl, 3-CH_3	4-Cl	135–137	80	67	1330, 1140	1090,935	1035
IIx	5-Cl, 2-CH_3	H	98–99.5	74	55	1315,1135	1095,925	1030

*Satisfactory elemental analysis were obtained C ± 0.25%, H ± 0.15%.

TABLE II PMR Spectral data of II

Compd. No.	*^1H NMR ($CDCl_3$) δ (ppm)*				*Coupling constants (H_Z)*					
	H_A	H_B	H_M	H_N	J_{AB}	J_{AM}	J_{AN}	J_{BM}	J_{BN}	J_{MN}
IIa	2.56	2.48	1.62	1.30	5.05	8.35	6.50	5.30	9.98	4.40
IIc	2.58	2.50	1.65	1.34	5.55	8.40	6.50	5.34	10.00	4.42
IIf	2.52	2.42	1.60	1.38	5.50	8.32	6.52	5.30	9.96	4.46
IIi	2.54	2.44	1.62	1.35	5.58	8.30	6.50	5.36	9.98	4.40
IIk	2.56	2.46	1.63	1.36	5.54	8.38	6.52	5.32	10.00	4.45
IIo	2.60	2.52	1.66	1.34	5.60	8.40	6.54	5.35	10.05	4.48
IIq	2.62	2.50	1.64	1.35	5.56	8.38	6.55	5.38	10.02	4.44
IIt	2.55	2.42	1.60	1.32	5.62	8.36	6.56	5.40	9.98	4.46
IIw	2.58	2.48	1.63	1.37	5.65	8.34	6.58	5.32	10.04	4.50

TABLE III CMR Spectral data of II

Compd. No.	^{13}C NMR ($CDCl_3$) δ (ppm)			
	C-1	C-2	C-3	Substituents
IIa	37.52	22.65	13.25	-
IIc	37.96	22.77	13.50	-
IIf	37.50	22.62	13.44	21.44 (SO_2Ph-CH_3)
IIi	37.55	22.68	13.36	54.96 (SO_2Ph-OCH_3)
IIk	37.98	22.76	13.38	55.10 (SO_2Ph-OCH_3)
IIo	37.99	22.78	13.52	-
IIq	37.80	22.80	13.54	-
IIt	37.88	22.82	13.48	21.32 (SO_2Ph-4-Cl-3-CH_3)
IIw	37.98	22.84	13.56	21.40 (SO_2Ph-4-Cl-3-CH_3)

General Procedure for the preparation of 1-arylsulfonyl-2-arylcyclopropanes (II)

Method A

A mixture of **I**[18,19] (10 mmol), trimethylsulfoxonium iodide (11 mmol), 50% aq. sodium hydroxide solution (25 ml) methylene chloride (25 ml) were stirred till a clear two-phase system was obtained. Benzyltriethylammonium chloride (BTEAC) (100 mg) was then added and continued stirring for a period of 2–3 h. Progress of the reaction was monitored by TLC. After completion of the reaction, it was diluted with water (100 ml) and the organic layer was separated, washed with water, brine and dried. Evaporation of the solvent gave a syrupy substance in most of the cases which was solidified on treatment with 2-propanol. The product on recrystallization yielded pure **II.**

Method B

A mixture of **I** (10 mmol) and trimethylsulfoxonium iodide (11 mmol) in dry dimethylsulfoxide (15 ml) was stirred until a clear solution was obtained. To this potassium t-butoxide (20 mmol) in dry dimethylsulfoxide (10 ml) was added dropwise at room temperature. After complete addition,

the reaction mixture was stirred for a additional 1 h. diluted with more water and stirred overnight, or until the product separated. This on recrystallization from 2-propanol resulted pure **II.**

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References

[1] A. Padwa, C. S. Chow, R. Rosenthal and L. W. Terry, *J. Org. Chem.*, **53,** 4193 (1988).

[2] A. Greenberg and J. F. Liebman, *Strained Organic Molecules,* Academic Press, New York (1979).

[3] A. De Meijere, *Angew Chem. Int. Ed. Engl.*, **18,** 809 (1979).

[4] H. N. C. Wong, M. Y. Hon, C. W. Tse, Y. C. Yip, J. Tanko and T. Hudlicky, *Chem. Rev.*, **89,** 165 (1989) and references cited therein.

[5] R. O. Robin Jr, J. R. Williams and G. W. Anderson, *J. Am. Chem. Soc.*, **63,** 1930 (1941).

[6] B. M. Trost and L. S. Melvin Jr, *Sulfur Ylides,* Academic Press, New York (1975).

[7] D. Bhaskar Reddy, T. Balaji and B. V. Ramana Reddy, *Phosphorus and Sulfur,* **17,** 297 (1983).

[8] M. V. Ramana Reddy, S. Reddy and P. V. Ramana Reddy, D. Bhaskar Reddy and N. Subba Reddy, *Phosphorus, Sulfur and Silicon,* **44,** 123 (1989).

[9] D. Bhaskar Reddy, P. V. Ramana Reddy, V. Padmavathi and M. V. Ramana Reddy, *Sulfur Lett.*, **13,** 83 (1991).

[10] E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **87,** 2025 (1965).

[11] E. V. Dehmlov and S. S. Dehmlov, *Phase Transfer Catalysis,* 3rd edition Weinheim, (1993).

[12] W. P. Heber and G. W. Gokel, *Phase Transfer Catalysis in Organic Synthesis,* Springer-Verlag, New York (1977).

[13] W. E. Truce and V. V. Badiger, *J. Org. Chem.*, **29,** 3277 (1964).

[14] W. E. Truce and C. T. Goralski, *J. Org. Chem.*, **34,** 3324 (1969).

[15] C. T. Goralski, *J. Org. Chem.*, **37,** 2d355 (1972).

[16] D. Bhaskar Reddy, P. V. Ramana Reddy, S. Vijayalakshmi and M. V. Ramana Reddy, *Phosphorus, Sulfur and Silicon.*, **84,** 63 (1993).

[17] G. L. Closs, R. A. Moss and J. J. Coyle, *J. Am. Chem. Soc.*, **78,** 4496 (1956).

[18] D. Bhaskar Reddy, B. Sankaraiah and T. Balaji, *Indian J. Chem.*, **19B,** 563 (1980) and references cited therein.

[19] D. Bhaskar Reddy, B. Sankaraiah and T. Balaji, *Phosphorus and Sulfur,* **16,** 293 (1983).