

## Note

### Carbenoid addition to $\alpha$ , $\beta$ -ethylenic sulfones under PTC—A stereospecific synthesis

D Bhaskar Reddy\*, K Ramachandra Reddy & A Padmaja  
Department of Chemistry, S V University, Tirupati 517 502,  
India

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Cyclopropanation of aryl styryl sulfones **1** with arylthiocarbene and chlorocarbene under PTC conditions results in the formation of 1, 2-diarylsulfonyl-3-arylcyclopropanes **3** and 1-arylsulfonyl-2-aryl-3, 3-dichlorocyclopropanes **4** respectively. The latter have been characterized by spectral parameters.

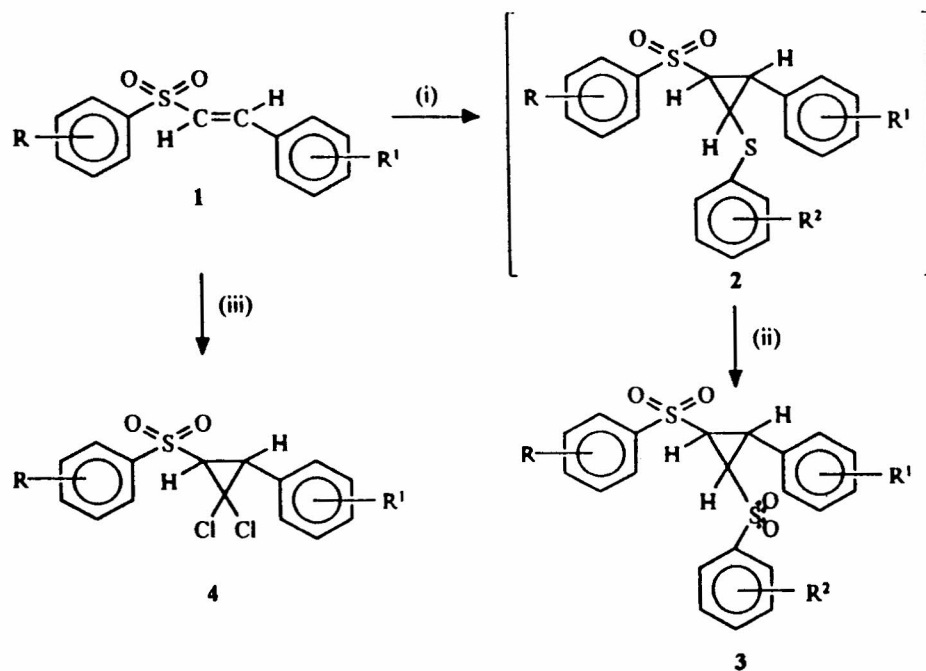
Amongst the various methods known for the synthesis of cyclopropanes, cycloaddition of carbenes to ethylenic systems has been found to be a versatile technique<sup>1-4</sup>. The carbenes are highly unstable and are generated *in situ* necessitating an inert medium and rigorous reaction conditions<sup>1</sup>. On the other hand, the addition of halocarbenes to olefins proceeds through an intermediate trihalocarbanion which displays an increased reactivity towards the double bond as compared to halogen free carbanion<sup>5</sup>. Carbenes as well as dihalocarbenes add to olefins in a stereospecific manner<sup>1,6</sup>. The generation of dihalocarbenes<sup>5,7,8</sup> and arylthiocarbene<sup>9-12</sup> *in situ* normally requires anhydrous conditions in order to avoid their rapid hydrolysis but under phase transfer conditions they display an enhanced reactivity since they are formed in the vicinity of reactant. In fact, several substituted alkenes were cyclopropanated with phenylthio and halocarbenes under phase transfer conditions<sup>13-16</sup>. However, exploitation of  $\alpha$ ,  $\beta$ -ethylenic sulfones for this purpose is limited. Our sustained interest in this field led us to report the cyclopropanation of aryl styryl sulfones with arylthiocarbene and dichlorocarbene adopting phase transfer conditions. Thus 1, 2-diarylsulfonyl-3-arylcyclopropanes **3** and 1-arylsulfonyl-2-aryl-3, 3-dichlorocyclopropanes **4** have been obtained by the cycloaddition of arylthiocarbene and dichlorocarbene to aryl styryl sulfones **1** respectively (Scheme I, Table I). The substrates used in the present study are considered to possess *E*-

geometry<sup>17</sup>. Hence, the addition of dichloro/arylthiocarbene generated *in situ* to the substrates furnished *trans* products, thus retaining the geometry of the former<sup>6,9,10</sup>. Many a time a number of side reactions would occur but a careful monitoring of the reaction process under phase transfer conditions lead to their successful synthesis.

The IR spectra of compounds **3** and **4** exhibited strong bands in the region 1030-1010  $\text{cm}^{-1}$  characteristic of cyclopropane ring deformation mode (Table I) and at 1110-1090 and 950-920  $\text{cm}^{-1}$  indicating *E*-geometry<sup>10,18</sup>. They also displayed strong bands in the region 1335-1310 and 1145-1115  $\text{cm}^{-1}$  for asymmetric and symmetric stretching vibrations of sulfonyl group. In compounds **4**, the spectra also contained bands due to C-Cl in the region 775-750  $\text{cm}^{-1}$  (ref. 19).

The <sup>1</sup>H NMR spectra of **3** exhibited an AMX pattern for cyclopropyl ring protons (Figure 1) and each one of them appeared as doublet of doublet at 3.85-3.94 ( $H_A$ ), 3.48-3.68 ( $H_M$ ) and 3.32-3.42 ppm ( $H_X$ ) (Table I). The signal at higher  $\delta_H$  value is assigned to  $H_A$  which is more deshielded than  $H_M$  and  $H_X$  (ref. 20). In general, in substituted cyclopropanes all substituents tend to cause protons *cis* to them to appear at higher fields than those *trans* to them<sup>21</sup>. Thus amongst  $H_M$  and  $H_X$ , the  $H_M$  appeared at downfield region relative to  $H_X$  as the former is *trans* to aryl moiety at C-3. A perusal of the *J* values from the Table I indicates that the geometry assigned to cyclopropane ring is in conformity with such assignments. In the case of **4** the cyclopropyl ring protons exhibit an AX splitting pattern (Figure 2). The methine protons  $H_A$  and  $H_X$  appeared as doublets at 3.56-3.72 and 3.38-3.58 ppm respectively. The higher  $\delta_H$  value is ascribed to  $H_A$  since it experiences deshielding effect and the *J* values indicate that they also possess *E*-geometry.

The 70 eV mass spectra of **3a** and **4a** indicates low intense molecular ion peaks at 398 and 326 respectively.  $\alpha$ -Cleavage process of the molecular ions is commonly observed. Stepwise elimination of SO<sub>2</sub> or phenylsulfonic acid moiety is a unique feature observed in the fragmentation of molecular ion **3a**<sup>16</sup>. However, in case of **4a** moderate intense peaks due to M+1, M-Cl and M-Cl<sub>2</sub> are observed. Peaks corresponding to M+2 and M+4 were also observed due to Cl<sup>37</sup> isotope.



( I )  $\text{R}^2 \text{ C}_6\text{H}_4\text{SCH}_2\text{Cl}/50\% \text{ aq. NaOH/BTEAC/CH}_2\text{Cl}_2$

( ii )  $\text{H}_2\text{O}_2/\text{AcOH}$

( iii )  $\text{CHCl}_3/50\% \text{ aq. NaOH/BTEAC/CH}_2\text{Cl}_2$

	R	R <sup>1</sup>	R <sup>2</sup>		R	R <sup>1</sup>	
III	a	H	H	IV	a	H	
	b	H	H		b	H	4-CH <sub>3</sub>
	c	H	H		c	H	4-Cl
	d	H	4-CH <sub>3</sub>		d	H	3,4-(OCH <sub>3</sub> ) <sub>2</sub>
	e	4-CH <sub>3</sub>	4-CH <sub>3</sub>		e	4-CH <sub>3</sub>	H
	f	4-CH <sub>3</sub>	4-CH <sub>3</sub>		f	4-CH <sub>3</sub>	4-Cl
	g	4-CH <sub>3</sub>	4-Cl		g	4-OCH <sub>3</sub>	H
	h	4-Cl	H		h	4-OCH <sub>3</sub>	4-OCH <sub>3</sub>
	i	4-Cl	H		i	4-Cl	H
	j	4-Cl	H		j	4-Cl	3,4-(OCH <sub>3</sub> ) <sub>2</sub>
				k	4-Br	H	
				l	4-Br	4-Cl	
				m	3,4 -Cl <sub>2</sub>	H	
				n	4-Cl,3-CH <sub>3</sub>	H	
				o	5-Cl,2-CH <sub>3</sub>	H	

Scheme I

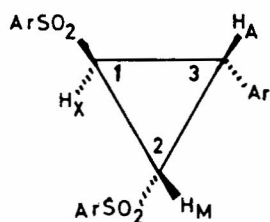


Figure 1

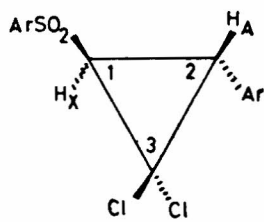


Figure 2

### Experimental Section

Melting points were determined on a Mel-Temp apparatus and are uncorrected. The IR spectra (KBr) were recorded on a Perkin-Elmer grating infrared spectrophotometer model 337, <sup>1</sup>H NMR spectra on a Bruker spectrospin NMR spectrometer operating at 200 MHz with TMS as an internal standard and mass spectra on Jeol JMS-D 300 mass spectrometer at 70 eV. The microana-

Table I—Characterization data of the compounds **3a-j** and **4a-o**

Compd	Yield (%)	m.p. (°C)	Mol. formula	IR (KBr) cm <sup>-1</sup>		<sup>1</sup> H NMR (CDCl <sub>3</sub> , δ, ppm)			Coupling constants (Hz)		
				SO <sub>2</sub>	Ring deformation mode	H <sub>A</sub>	H <sub>M</sub>	H <sub>X</sub>	J <sub>AM</sub>	J <sub>AX</sub>	J <sub>MX</sub>
<b>3a</b>	64	135-36	C <sub>21</sub> H <sub>18</sub> S <sub>2</sub> O <sub>4</sub>	1310, 1125	1025	3.89	3.54	3.36	9.85	6.80	4.90
<b>3b</b>	62	143-44	C <sub>22</sub> H <sub>20</sub> S <sub>2</sub> O <sub>4</sub>	1315, 1125	1020	3.86	3.48	3.37	9.85	6.82	4.94
<b>3c</b>	68	167-68	C <sub>21</sub> H <sub>17</sub> S <sub>2</sub> O <sub>4</sub> Cl	1325, 1130	1020	3.91	3.62	3.39	9.80	6.79	4.92
<b>3d</b>	72	183-84	C <sub>22</sub> H <sub>19</sub> S <sub>2</sub> O <sub>4</sub> Cl	1315, 1120	1025	—	—	—	—	—	—
<b>3e</b>	60	226-27	C <sub>23</sub> H <sub>22</sub> S <sub>2</sub> O <sub>4</sub>	1320, 1125	1020	3.85	3.56	3.32	9.84	6.80	4.94
<b>3f</b>	65	234-35	C <sub>24</sub> H <sub>24</sub> S <sub>2</sub> O <sub>4</sub>	1315, 1115	1015	—	—	—	—	—	—
<b>3g</b>	70	197-98	C <sub>22</sub> H <sub>17</sub> S <sub>2</sub> O <sub>4</sub> Cl	1325, 1125	1030	3.94	3.52	3.35	9.85	6.81	4.90
<b>3h</b>	75	247-49	C <sub>21</sub> H <sub>17</sub> S <sub>2</sub> O <sub>4</sub> Cl	1320, 1120	1025	—	—	—	—	—	—
<b>3i</b>	64	189-90	C <sub>22</sub> H <sub>19</sub> S <sub>2</sub> O <sub>4</sub> Cl	1325, 1130	1020	—	—	—	—	—	—
<b>3j</b>	68	258-59	C <sub>21</sub> H <sub>16</sub> S <sub>2</sub> O <sub>4</sub> Cl <sub>2</sub>	1325, 1125	1025	3.90	3.68	3.42	9.82	6.80	4.93
<b>4a</b>	58	145-46	C <sub>15</sub> H <sub>12</sub> SO <sub>2</sub> Cl <sub>2</sub>	1320, 1140	1020	—	—	—	—	—	—
<b>4b</b>	62	164-65	C <sub>16</sub> H <sub>14</sub> SO <sub>2</sub> Cl <sub>2</sub>	1320, 1145	1015	3.60	—	3.50	—	4.80	—
<b>4c</b>	65	158-59	C <sub>15</sub> H <sub>11</sub> SO <sub>2</sub> Cl <sub>3</sub>	1325, 1150	1025	3.68	—	3.52	—	4.81	—
<b>4d</b>	60	169-70	C <sub>17</sub> H <sub>16</sub> SO <sub>4</sub> Cl <sub>2</sub>	1315, 1125	1010	—	—	—	—	—	—
<b>4e</b>	59	153-54	C <sub>16</sub> H <sub>14</sub> SO <sub>2</sub> Cl <sub>2</sub>	1325, 1125	1015	3.56	—	3.52	—	4.81	—
<b>4f</b>	64	172-74	C <sub>16</sub> H <sub>13</sub> SO <sub>2</sub> Cl <sub>3</sub>	1325, 1145	1020	3.59	—	3.58	—	4.82	—
<b>4g</b>	66	168-69	C <sub>16</sub> H <sub>14</sub> SO <sub>3</sub> Cl <sub>2</sub>	1320, 1130	1010	3.62	—	3.54	—	4.82	—
<b>4h</b>	60	149-50	C <sub>17</sub> H <sub>16</sub> SO <sub>4</sub> Cl <sub>2</sub>	1320, 1135	1020	—	—	—	—	—	—
<b>4i</b>	63	183-84	C <sub>15</sub> H <sub>11</sub> SO <sub>2</sub> Cl <sub>3</sub>	1335, 1145	1025	—	—	—	—	—	—
<b>4j</b>	65	192-94	C <sub>17</sub> H <sub>15</sub> SO <sub>4</sub> Cl <sub>3</sub>	1335, 1140	1020	—	—	—	—	—	—
<b>4k</b>	68	143-44	C <sub>15</sub> H <sub>11</sub> SO <sub>2</sub> Cl <sub>2</sub> Br	1330, 1135	1020	3.72	—	3.54	—	4.81	—
<b>4l</b>	62	165-66	C <sub>15</sub> H <sub>10</sub> SO <sub>2</sub> Cl <sub>3</sub> Br	1335, 1145	1025	—	—	—	—	—	—
<b>4m</b>	65	169-71	C <sub>15</sub> H <sub>10</sub> SO <sub>2</sub> Cl <sub>4</sub>	1335, 1140	1015	3.66	—	3.38	—	4.80	—
<b>4n</b>	58	144-45	C <sub>16</sub> H <sub>13</sub> SO <sub>2</sub> Cl <sub>3</sub>	1325, 1135	1010	—	—	—	—	—	—
<b>4o</b>	64	139-40	C <sub>16</sub> H <sub>13</sub> SO <sub>2</sub> Cl <sub>3</sub>	1330, 1130	1020	—	—	—	—	—	—

Satisfactory elementary analyses were obtained C ± 0.36, H ± 0.18.

lyses were performed at CECRI, Karaikudi. Purity of the compounds was checked by TLC using silica gel H(BDH) and hexane-ethyl acetate (3:2) as an eluant.

### 1, 2-Diarylsulfonyl-3-arylcyclopropanes **3**:

**General procedure.** A mixture of aryl styryl sulfone (5 mmol)<sup>21,22</sup> **1** and aryl chloromethyl sulfide<sup>12</sup> (6 mmol) in methylene chloride (30 mL) and 50% aq. NaOH (20 mL) was stirred well to obtain a clear two-phase system. Then, benzyltriethylammonium chloride (BTEAC) (100 mg) was added and stirring was continued at room temperature for 10-12 hr. After completion of the reaction, the contents were diluted with water. The organic layer separated was washed with water, brine and then dried. Removal of the solvent gave crude thiocyclopropanes **2** as viscous liquids which were subsequently oxidized with 10 mL of 30% hydrogen peroxide (10 mL) in glacial acetic

acid (20 mL) at reflux temperature. The contents were allowed to cool and poured onto crushed ice with stirring. The solid separated was collected, washed with water, dried and recrystallized from ethanol or 2-propanol to obtain pure **3**.

### 1 - Arylsulfonyl - 2 - aryl - 3, 3 - dichlorocyclopropanes **4**: **General procedure.**

A mixture of aryl styryl sulfone **1** (5 mmol) and chloroform (50 mL) was stirred with 50% aq. NaOH (20 mL) till a clear two-phase system was obtained. To this, benzyltriethylammonium chloride (BTEAC) (100 mg) was added and the mixture stirred at 45°C for 8-10 hr. The progress of the reaction was monitored by TLC. The contents were diluted with water and the organic layer separated was washed with water, brine and dried. Evaporation of the solvent gave a solid which was recrystallized from benzene or glacial acetic acid to get pure **4**.

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