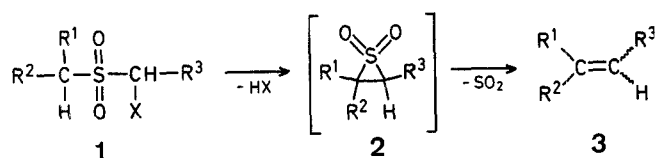


### The Phase-Transfer Catalyzed Ramberg-Bäcklund Reaction

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The Ramberg-Bäcklund rearrangement of  $\alpha$ -halo sulfones **1** (Scheme A) has proven to be an exceptionally efficient and versatile method for the preparation of olefins **3**<sup>1,2</sup>. The importance of this procedure has increased in recent years as new methods for the preparation of  $\alpha$ -bromo and  $\alpha$ -chloro sulfones have appeared<sup>2</sup>. The reaction is generally carried out in aqueous sodium hydroxide solution for water-soluble substrates and in either sodium methoxide/methanol or water/dioxan mixtures for less polar substrates.



Scheme A

The choice of base and solvent is not trivial; Paquette et al.<sup>3</sup> have reported that some  $\alpha$ -halo sulfones which are inert to prolonged heating with 2 normal sodium hydroxide in dioxan, are readily rearranged with potassium *t*-butoxide in tetrahydrofuran. It was suggested that the inertness in aqueous solvents was due to the lack of conformational freedom at the highly solvated  $\alpha$ -sulfonyl carbanion site.

It appeared to us that there might be several advantages in carrying out the  $\alpha$ -halo sulfone rearrangement under phase transfer conditions. Firstly, the use of halocarbon solvents such as dichloromethane would allow a wide range of non-polar  $\alpha$ -halo sulfones to be reacted and permit simple isolation of olefinic products. Secondly, we anticipated that the

rearrangement could be carried out under very mild conditions, as the  $\alpha$ -sulfonyl carbanion should form readily, in analogy with previous work<sup>4</sup> on the condensation of sulfones and aldehydes under PTC conditions. The  $\alpha$ -sulfonyl carbanion should be highly reactive, due to the lack of powerful solvation factors in the organic layer, and quickly close to the episulfone intermediate **2**. Thirdly, we felt that reaction conditions should allow certain base-sensitive functionality, e.g., esters, within the  $\alpha$ -halo sulfone to maintain their integrity throughout the course of reaction and work-up.

We have found that when the  $\alpha$ -halo sulfones **1** shown in the Table were dissolved in dichloromethane and treated with aqueous sodium hydroxide in the presence of a phase transfer catalyst, the Ramberg-Bäcklund reaction occurred readily to afford the expected olefin **3** in high yield. The reaction proceeded faster in the case of those sulfones possessing benzylic hydrogens than in the one case, i.e., chloromethyl cyclohexyl sulfone (**1b**), where a tertiary hydrogen would be abstracted. This was reflected in the observation that **1a**, **1c**, **1d**, and **1e** were rearranged to olefins with 10% sodium hydroxide at room temperature while **1b** required heating at reflux and the use of 20% sodium hydroxide. It is noteworthy that even a 1% sodium hydroxide solution was a strong enough base to bring about the rearrangement of benzyl chloromethyl sulfone (**1a**).

Both Aliquat-336 (tricaprylmethylammonium chloride) and TEBA (benzyltriethylammonium chloride) were found to be effective at bringing about the rearrangement when used at a concentration of 10 mol% relative to  $\alpha$ -halo sulfone. No rearrangement was observed for any compound in the absence of the phase-transfer catalyst. As shown in the Table for both **1a** and **1b**, Aliquat-336 appeared to cause the rearrangement to occur at a faster rate than did TEBA, however, the yield of olefinic product at the end of reaction was virtually identical for both catalysts. The faster rate found for Aliquat-336 apparently reflects its more favorable partitioning characteristics in this system. In light of the facility with which Aliquat-336 catalyzes the above rearrangement, it is noteworthy that the expectation for ester function stability under these conditions was confirmed by rearrangement of ethyl  $\alpha$ -benzylsulfonyl- $\alpha$ -bromoacetate (**1d**) to ethyl cinnamate (**2d**) in excellent yield.

Recently, Meyers et al.<sup>10,11</sup> have described a "one-flask" alternative to the standard Ramberg-Bäcklund procedure in which the  $\alpha$ -halo sulfone is formed *in situ* by treatment of the sulfone with potassium hydroxide, *t*-butyl alcohol, and carbon tetrachloride. The main synthetic drawbacks of this procedure appear to be that side products may arise from simultaneous generation of dichlorocarbene and that other base-sensitive functionality within the molecule may not survive reaction conditions. We have found that treatment of dibenzyl sulfone (**1g**) in dichloromethane containing carbon tetrachloride with 10% aqueous

Table. Olefins **3** from  $\alpha$ -Halo Sulfones **1**

Sulfone No.	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	X	Reaction Conditions Base/Catalyst/Time/Temp.	Yield [%] of <b>3</b>		b.p. [°C]/torr or m.p. [°C]	
						G.L.C. <sup>a</sup>	Isolated <sup>b</sup>	found	reported
<b>1a</b> <sup>5</sup>	C <sub>6</sub> H <sub>5</sub>	H	H	Cl	10% NaOH/Aliquat-336/1.5 h/r.t.	89	82	143–145°/760	145.2°/760 <sup>12</sup>
					1% NaOH/Aliquat-336/1.5 h/r.t.	25			
					10% NaOH/TEBA/5 h/r.t.	85	80		
					1% NaOH/TEBA/1.5 h/r.t.	<5			
					4 normal NaOCH <sub>3</sub> /CH <sub>3</sub> OH/1 h/80°C		78		
<b>1b</b> <sup>6</sup>	—(CH <sub>2</sub> ) <sub>5</sub> —	H	H	Cl	20% NaOH/Aliquat-336/40 h/reflux	92	86 <sup>c</sup>	99–101°/760	97–99°/760 <sup>6</sup>
					20% NaOH/Aliquat-336/4 h/r.t.	10			
					20% NaOH/TEBA/40 h/reflux	90			
					20% NaOH/TEBA/4 h/r.t.	<5			
					25% NaOH/24 h/reflux		80 <sup>b</sup>		
<b>1c</b> <sup>6</sup>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	H	H	Cl	20% NaOH/Aliquat-336/30 h/reflux	93	85	91–93°/760	92–94°/760 <sup>6</sup>
					20% NaOH/TEBA/30 h/reflux	88			
					25% NaOH/24 h/reflux		78 <sup>c</sup>		
<b>1d</b> <sup>7</sup>	C <sub>6</sub> H <sub>5</sub>	H	COOC <sub>2</sub> H <sub>5</sub>	Br	10% NaOH/Aliquat-336/2 h/r.t. 4 normal NaOC <sub>2</sub> H <sub>5</sub> /C <sub>2</sub> H <sub>5</sub> OH/0.5 h/80°C	83	75 79 <sup>c,7</sup>	140–142°/15	144°/15 <sup>12</sup>
<b>1e</b> <sup>8</sup>	C <sub>6</sub> H <sub>5</sub>	H	C <sub>6</sub> H <sub>5</sub>	Br	10% NaOH/Aliquat-336/2 h/r.t. 0.68 molar NaOCH <sub>3</sub> /CH <sub>3</sub> OH/5 h, 25°C	94	89 89 <sup>8</sup>	122–124° <sup>d</sup>	124.5–124.8° <sup>12</sup>
<b>1f</b> <sup>9</sup>	C <sub>6</sub> H <sub>5</sub>	H	C <sub>6</sub> H <sub>5</sub>	Cl	10% NaOH/Aliquat-336/2 h/r.t. 2 normal NaOH/H <sub>2</sub> O/dioxan/0.5 h/reflux	91	88 94 <sup>9</sup>	122–124° <sup>d</sup>	124.5–124.8° <sup>12</sup>
<b>1g</b>	C <sub>6</sub> H <sub>5</sub>	H	C <sub>6</sub> H <sub>5</sub>	H	10% NaOH/Aliquat-336/1.5 h/reflux	99	94	122–124° <sup>d</sup>	124.5–124.8° <sup>12</sup>
					10% NaOH/Aliquat-336/1 h/r.t.	20			
					10% NaOH/TEBA/1.5 h/reflux	<5			
					Sat. Na <sub>2</sub> CO <sub>3</sub> /Aliquat-336/48 h/reflux		70		
					Sat. NaHCO <sub>3</sub> /Aliquat-336/48 h/reflux		59		
					KOH powder/ <i>t</i> -C <sub>4</sub> H <sub>9</sub> OH/H <sub>2</sub> O/CCl <sub>4</sub> /1 h/25–80°C		100 <sup>10</sup>		

<sup>a</sup> Hewlett Packard Model 5710A Gas Chromatograph; 6' × 1/4" S.S. OV-17, 60–80 mesh, W. A. W. column.

<sup>b</sup> Dichloromethane as organic solvent.

<sup>c</sup> Yield of corresponding acid.

<sup>d</sup> Product is *trans*-1,2-diphenylethylene.

<sup>e</sup> Purity ≥ 99% by G.L.C., no evidence of contamination by 1-methylcyclohexene.

sodium hydroxide at reflux for 1.5 h in the presence of Aliquat-336 afforded a quantitative yield of the rearrangement product, *trans*-stilbene. Analogous treatment of **1g** in the absence of Aliquat-336 gave no reaction, while the use of TEBA under the same conditions gave only a low yield of *trans*-stilbene. Moderate yields of *trans*-stilbene were obtained when saturated aqueous solutions of sodium carbonate and sodium hydrogen carbonate were separately used with Aliquat-336.

In summary, we have found that  $\alpha$ -halo sulfones **1** readily undergo the Ramberg-Bäcklund rearrangement under phase-transfer catalysis conditions to afford olefinic products **2** in excellent yield. In addition, the *in situ* generation of  $\alpha$ -halo sulfones, utilizing base and carbon tetrachloride and subsequent rearrangement are accomplished in a similar manner. We expect that these techniques will be widely applicable for the rearrangement of suitable sulfones.

**Styrene (2a) from Benzyl Chloromethyl Sulfone (1a); Typical Procedure:**

To sulfone **1a** (20.4 g, 0.1 mol) dissolved in dichloromethane (340 ml) are added 10% aqueous sodium hydroxide (170 ml) and the phase-transfer catalyst (0.01 mol). The reaction mixture is then stirred vigorously with a magnetic bar and the progress of the reaction is monitored by analysis of the organic layer by gas chromatography and thin layer chromatography. When reaction is complete, the organic phase is separated, washed with water, saturated sodium chloride solution, and then dried with anhydrous sodium sulfate. The solvent is distilled carefully through a 24 inch Vigreux column and the product collected by distillation through a 5 inch Vigreux column; yield: 8.5 g (82%); b.p. 145–146 °C.

***trans*-Stilbene from Dibenzyl Sulfone (1g):**

To sulfone **1g** (5.0 g, 0.02 mol) dissolved in dichloromethane (100 ml) and carbon tetrachloride (50 ml) are added 10% aqueous sodium hydroxide solution (100 ml) and Aliquat-336 (1.0 g, 2 mmol). This mixture is stirred vigorously and heated at reflux for 1.5 h. The reaction mixture is then cooled, and the organic phase is separated, washed twice with water, once with saturated sodium chloride solution, and then dried with anhydrous sodium sulfate. The drying agent is filtered off and the solvent stripped to afford *trans*-stilbene as a white solid; yield: 3.6 g (94%); m.p. 122–124 °C.

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