

# Communications

## Some Carbanionic Reactions of Halomethyl Aryl Sulfones<sup>1</sup>

**Summary:** Chloro- and bromomethyl aryl sulfones are easily converted into carbanions in the presence of concentrated aqueous sodium hydroxide and quaternary ammonium catalyst. These carbanions are readily alkylated and condense with carbonyl compounds giving oxiranes. The same conditions can be applied for alkylation of dihalomethyl aryl sulfones.

**Sir:** Halomethyl sulfones should form carbanions relatively easily, since both sulfonyl group and halogen atom act as carbanion-stabilizing substituents. There are, however, only a few papers describing reactions of these carbanions. Thus Truce, *et al.*,<sup>2</sup> reported alkylation of bromomethyl-sulfone carbanions with trialkylboranes in the presence of potassium *tert*-butoxide in THF-*tert*-butyl alcohol solvents. Potassium *tert*-butoxide<sup>3</sup> and NaH<sup>4</sup> have also been applied in the synthesis of  $\alpha$ -sulfonyloxiranes from chloro- and bromomethyl aryl sulfones and carbonyl compounds.

We have found that aqueous concentrated sodium hydroxide in the presence of a quaternary ammonium salt catalyst<sup>5</sup> (we use triethylbenzylammonium chloride-TEBA) can be used efficiently for the generation of  $\alpha$ -halo-sulfonyl carbanions and for a variety of their reactions, some of which have not been described previously.

Thus chloromethyl<sup>6</sup> and bromomethyl *p*-tolyl sulfones<sup>7</sup> are readily alkylated under these conditions with mono- and dihaloalkanes giving  $\alpha$ -haloalkyl or  $\alpha$ -halocycloalkyl *p*-tolyl sulfones in high yields.

Although the starting sulfones contain an active methylene group only negligible dialkylation is observed. However, the alkylation is sometimes accompanied by dehydrohalogenation leading to  $\alpha,\beta$ -unsaturated sulfones. This reaction occurs particularly easily in cases in which allyl or benzyl groups have been introduced. Thus, carrying out the alkylation under somewhat elevated temperature, it is possible to prepare directly the unsaturated sulfones.

Some dihaloalkanes are able to substitute both hydrogen atoms in halomethyl sulfones giving  $\alpha$ -halocycloalkyl sulfones (Scheme I).

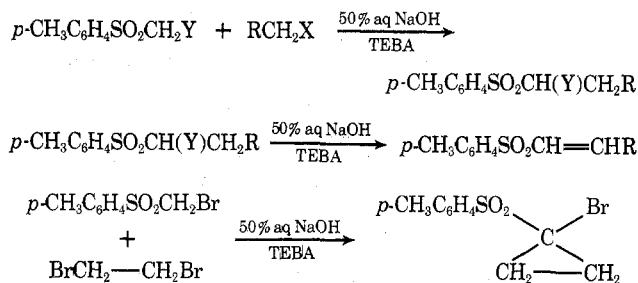
The  $\alpha$ -halosulfonyl carbanions generated under the catalytic two-phase conditions react with aldehydes and ketones giving corresponding sulfonyl-substituted oxiranes (Scheme II). The yields of these oxiranes are high, often ~90%. In the case of aldehydes the trans epoxide isomers are the only products isolated. The sulfonyloxiranes are reported<sup>8</sup> to be of limited stability, rearranging easily into  $\alpha$ -sulfonyl aldehydes.

However, the rather mild conditions in which the condensation takes place allow one in almost all cases, but that of acetophenone, to isolate pure oxirane.

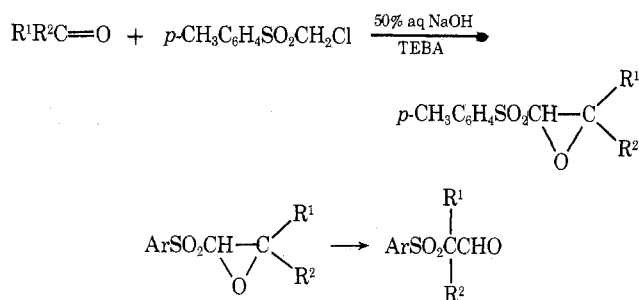
Aldehydes, being strong electrophiles, are able to react with halomethyl *p*-tolyl sulfones in the presence of concentrated aqueous sodium hydroxide without a catalyst. Owing to complete mutual insolubility of the phases, this reaction is believed to proceed directly at the phase boundary. Similar phenomena have been already observed.<sup>9</sup>

Dihalomethyl sulfones should be still stronger C-H acids as compared with monohalomethyl analogs. However, their carbanionic reactions are almost unknown. The case re-

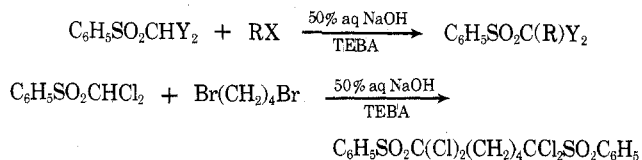
### Scheme I



### Scheme II



### Scheme III



ported by Hine,<sup>10</sup> formation of difluorocarbene by base-induced decomposition of difluoromethyl phenyl sulfone, which appears to proceed *via* the corresponding carbanion, is to our knowledge the only example.

Readily accessible dihalomethyl aryl sulfones,<sup>11</sup> in the presence of aqueous sodium hydroxide and a quaternary ammonium salt catalyst, are easily converted into the corresponding dihalomethyl sulfonyl carbanions, being efficiently alkylated with various alkyl halides (Scheme III). The reaction with  $\alpha,\omega$ -dihaloalkanes leads to the corresponding  $\alpha,\omega$ -dihalo sulfonylalkanes.

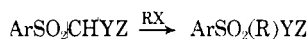
Some examples of alkylated halomethyl sulfones and sulfonyloxiranes are presented in Tables I and II.

The procedures for both reactions are very simple. Examples follow.

**1.  $\alpha$ -Bromopropyl *p*-Tolyl Sulfone.** Bromomethyl *p*-tolyl sulfone (2.0 g, 8 mmol), ethyl bromide (0.96 g, 8.8 mmol), 50% aqueous sodium hydroxide (15 ml), and TEBA (0.05 g) were vigorously stirred at 30–35° for 1 hr (mild exothermic effect). The mixture was diluted with water and the product was isolated and purified by recrystallization from ethanol (Table I, first entry).

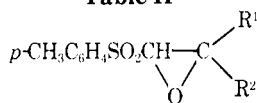
**2. *trans*-Styryl *p*-Tolyl Sulfone.** The procedure is as described above; benzyl chloride was used instead of ethyl bromide. The reaction was carried out at 85–90° for 1 hr, yield 70%, mp 119–121° (lit.<sup>14</sup> mp 121–122°).

**3. 2,2-Dimethyl-3-*p*-tolylsulfonyloxirane.** Chloromethyl *p*-

Table I<sup>12</sup>

Ar	Y	Z	RX	Yield, %	Mp, °C <sub>i</sub>
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	H	Br	C <sub>2</sub> H <sub>5</sub> Br	67	98–100
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	H	Br	C <sub>4</sub> H <sub>9</sub> Br	68	41–42 <sup>a</sup>
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	H	Cl	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	60	79–81 <sup>b</sup>
C <sub>6</sub> H <sub>5</sub>	Cl	Cl	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	84	145–147
C <sub>6</sub> H <sub>5</sub>	Cl	Cl	C <sub>2</sub> H <sub>5</sub> Br	72	74–76
C <sub>6</sub> H <sub>5</sub>	Br	Br	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	75	168–170
1- <i>p</i> -Tolylsulfonyl-1-bromocyclopropane				73	138–140
1,6-Di- <i>p</i> -tolylsulfonyl-1,1,6,6-tetrachlorohexane <sup>d</sup>				87	214.5–216

<sup>a</sup> Bp 146–149° (0.1 mm). <sup>b</sup> Lit.<sup>13</sup> mp 79–82°. <sup>c</sup> Alkylation with ethylene dibromide. <sup>d</sup> Molar ratio of dichloro sulfone to dibromobutane 2:1.

Table II<sup>12</sup>

R <sup>1</sup>	R <sup>2</sup>	Yield, %	Mp, °C	
			Obtained	Lit. <sup>3</sup>
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	90	105–107	106–107
CH <sub>3</sub>	CH <sub>3</sub>	91	94–95	93.5–94
C <sub>6</sub> H <sub>5</sub>	H	60	153–154	157–159 dec
(CH <sub>3</sub> ) <sub>2</sub> CH	H	65	82–84	
(CH <sub>2</sub> ) <sub>5</sub>		90	54–55	54–55

tolyl sulfone (3.06 g, 15 mmol), 50% aqueous sodium hydroxide (10 ml), acetonitrile (2 ml), TEBA (0.05 g), and acetone (1.04 g, 18 mmol) were stirred at 30–35° (mild exothermic effect) for 45 min. The product was isolated and purified by crystallization (carbon tetrachloride–hexane) (Table II, second entry).

4.  $\alpha,\alpha$ -Dichloropropyl Phenyl Sulfone. Dichloromethyl phenyl sulfone (2.25 g, 10 mmol), ethyl bromide (1.3 g, 12 mmol), 50% aqueous sodium hydroxide (10 ml), and TEBA (0.05 g) were vigorously stirred at 35–40° for 1 hr (exothermic effect). The mixture was diluted with water and the product was isolated and crystallized from methanol (Table I, fifth entry).

## References and Notes

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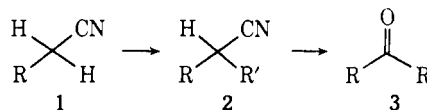
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## The Oxidative Decyanation of Secondary Nitriles via $\alpha$ -Hydroperoxynitriles

**Summary:** The oxidative decyanation of secondary nitriles to ketones was effected by trapping nitrile anions with molecular oxygen, reducing the resulting  $\alpha$ -hydroperoxynitriles to cyanohydrins with stannous chloride, and converting the cyanohydrins to ketones with sodium hydroxide.

**Sir:** To demonstrate the functional equivalence of primary nitriles 1 as acyl carbanion equivalents<sup>1</sup> required methodology for effecting the monoalkylation<sup>2</sup> of 1 and the oxidative decyanation of secondary nitriles 2 to ketones 3. Proce-



dures which accomplish the latter transformation (2  $\rightarrow$  3) effect the oxidation of nitriles to cyanohydrins *via* intermediate  $\alpha$ -chloro,<sup>3</sup>  $\alpha$ -iodo,<sup>4</sup> and  $\alpha$ -thiophenoxynitriles<sup>5</sup> and subsequent conversion of the cyanohydrins to ketones. Few procedures, however, allow for the direct introduction of an oxygen substituent  $\alpha$  to a nitrile.<sup>6</sup> We now wish to report a general oxidative decyanation procedure which realizes this objective.

Secondary nitrile anions 4 generated using lithium diisopropylamide trapped molecular oxygen at  $-78^\circ$  to afford lithium  $\alpha$ -cyanohydroperoxides 5. Quenching 5 with aqueous acid or acetyl chloride provided the isolable  $\alpha$ -hydroperoxynitrile<sup>7</sup> 6a or the acetate derivative 6b, respectively. The reduction of 5 with an acidic stannous chloride solution<sup>8</sup> furnished the cyanohydrin 7. Subsequent exposure of 7 to aqueous sodium hydroxide afforded the ketone 3 in good overall yield from the nitrile 2 (Table I).<sup>9</sup> For example, 2 (R = CH<sub>2</sub>Ph; R' = CH<sub>3</sub>) was sequentially converted to 6a, 7, and 3 in isolated yields of 92, 89, and 98%, respectively. In contrast to reported oxidative decyanation procedures,<sup>4,5</sup> this methodology was applicable to the synthesis of dialkyl ketones as well as alkyl aryl and diaryl ketones from 2. Primary nitriles 1 afforded only low yields of al-

