chloride, and 3.4 g of acetonitrile was heated with stirring at 110° for 2 hr and then cooled. Methanol (34 ml) was added to the cooled reaction mixture and the resulting solution was refrigerated. After standing under refrigeration for several days, no solid separated from the solution. The methanol was removed *in vacuo* leaving a thick, viscous, yellow oil. The oil was dissolved in a minimum amount of dry benzene and 12.87 g (0.127 mol) of triethylamine was added. The reaction mixture was stirred for 1 hr and then filtered to remove the triethylamine hydrochloride which had precipitated. The triethylamine hydrochloride was washed with several portions of dry benzene. The benzene was removed *in vacuo* from the combined benzene filtrates leaving a yellow oil which crystallized on addition of a small amount of 95% ethanol. The solid was filtered, dried, and recrystallized from 95% ethanol to give 9.90 g (45% yield) of β-(benzenesulfonyl)-*cis*-β-methylstyrene: mp 94.5–95.5°; nmr δ 2.10 (d, 3), 7.33 (s, 5), 7.45–7.70 (m, 3), 7.75–8.05 (m, 3).

*Anal.* Calcd for $C_{15}H_{14}O_2S$: C, 69.74; H, 5.46; S, 12.41. Found: C, 69.68; H, 5.23; S, 12.53.

**Attempted Reaction of Benzenesulfonyl Chloride with *trans*-Stilbene.**—A mixture of 18.00 g (0.10 mol) of *trans*-stilbene, 17.67 g (0.10 mol) of benzenesulfonyl chloride, 0.130 g (1.0 mmol) of anhydrous cupric chloride, 0.206 g (1.5 mmol) of triethylamine hydrochloride, and 4.00 g of acetonitrile was heated, with stirring, at 120° for 2 hr and then cooled. Methanol (40 ml) was added to the cooled reaction mixture and unreacted *trans*-stilbene separated as a pale yellow, crystalline solid. The recovered *trans*-stilbene was filtered, dried, and recrystallized from 95% ethanol to give 17.10 g (95% recovery), mp 125–126° (lit.[10] mp 124°).

**General Procedure for the Preparation of Unsaturated Sulfones (2).**—To a saturated solution of the sulfonyl chloride adduct 1 in dry benzene was added 1.5 equiv of triethylamine. The reaction mixture was allowed to stir for 45 min and then filtered to remove the triethylamine hydrochloride produced. The triethylamine hydrochloride was washed with several portions of dry benzene. The benzene was removed *in vacuo* from the combined benzene filtrates leaving an oil which crystallized on addition of a small amount of ethanol. The solid was recrystallized from 95% ethanol to give analytically pure 2.

**Reaction of α-Toluenesulfonyl Chloride (6) with Styrene.**—In a 100-ml, three-neck flask equipped with a magnetic stirrer, a nitrogen inlet tube, and a reflux condenser with a drying tube were placed 10.41 g (0.10 mol) of styrene, 19.06 g (0.10 mol) of α-toluenesulfonyl chloride, 0.130 g (0.0010 mol) of anhydrous cupric chloride, 0.206 g (0.0015 mol) of triethylamine hydrochloride, and 4.00 g of acetonitrile. The reaction mixture was heated, with stirring, at 125° for 2 hr and then cooled. During the entire 2-hr reaction period the evolution of sulfur dioxide ($SO_2$) was noted. Methanol (40 ml) was added to the cooled reaction mixture, and the resulting solution was refrigerated. A small amount of a white solid separated from the cold solution. The solid was filtered, dried, and recrystallized from 95% ethanol to give 0.85 g of 1-chloro-1-phenyl-2-(α-toluenesulfonyl)ethane, mp 121–122°.

*Anal.* Calcd for $C_{15}H_{15}ClO_2S$: C, 61.11; H, 5.13; Cl, 12.03; S, 10.88. Found: C, 61.23; H, 5.10; Cl, 11.76; S, 10.87.

The methanol was removed from the recrystallization liquor *in vacuo* leaving a yellow oil which was distilled under reduced pressure. The distillation yielded 7.18 g of a colorless liquid which was shown by nmr to be a mixture consisting of 65% benzyl chloride and 35% styrene. A heavy, dark residue remained after distillation. The residue was dissolved in 95% ethanol and decolorized. The ethanol solution was cooled yielding an additional 1.00 g of 1-chloro-1-phenyl-2-(α-toluenesulfonyl)-ethane, mp 118–119°. The total yield of 1:1 adduct was 1.85 g (6% yield).

**Registry No.**—5, 30246-74-3; 7, 30158-39-5.

**Acknowledgment.**—The authors wish to express their appreciation for financial support of this work by the Purdue Research Foundation and the Public Health Service Research Grant No. CA-04536-09 from the National Cancer Institute.

(10) "Handbook of Chemistry and Physics," 45th ed, Chemical Rubber Publishing, Cleveland, Ohio, 1964, p C-546.

## α,β-Epoxysulfonamides

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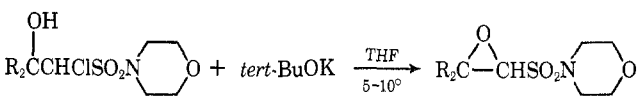
Although various electronegatively substituted epoxides are known, considerable current attention is being devoted to the synthesis of new moieties in this classification.[1] Only recently has the preparation of α,β-epoxysulfonyl and sulfinyl systems been reported.[2]

Our own interest in α-substituted sulfonic acid derivatives[3] coupled with the facile synthetic route to β-hydroxy-α-chlorosulfonamides, which we recently reported,[4] suggested the preparation of the novel α,β-epoxysulfonic acid derivatives.

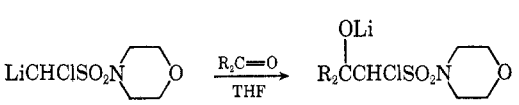
Indeed, when the precursory β-hydroxy-α-chlorosulfonamides **1** were treated with potassium *tert*-butoxide in THF, the α,β-epoxysulfonamides were formed in good to moderate yields (Table I).




**1** **2**

This reaction almost certainly proceeds *via* initial formation of the β-alkoxide followed by an intramolecular displacement of the halogen atom. The ease (low temperature, short reaction time) of this displacement is noteworthy since it is in direct contrast to intermolecular SN2 displacements α to sulfonyl groupings in both sulfones[5] and sulfonamides,[6] which occur only with difficulty. However, a parallel effect is encountered in the Ramberg–Bäcklund reaction, which also involves an intramolecular displacement α to a sulfonyl grouping and can also occur at low temperature.[7] Seemingly, when the nucleophilic center is generated in the proximity of the reaction site, the sulfonyl group exhibits either a highly diminished retarding effect or no retarding effect on α displacements.

It would be useful synthetically if the α,β-epoxide could be generated directly from the condensation of the α-chloroalkyllithium sulfonamide **6** with a ketone, thereby bypassing the isolation and subsequent ring closing of the β-hydroxy-α-chlorosulfonamide. However, allowing a solution of **6** and a ketone, *e.g.*, acetone,




**6** **7**

(1) (a) J. Cantacuzene and J.-M. Normant, *Tetrahedron Lett.*, 2947 (1970); (b) H. Newman and R. B. Angier, *Tetrahedron*, **26**, 825 (1970).

(2) (a) P. F. Vogt and D. F. Tavares, *Can. J. Chem.*, **47**, 2875 (1969); (b) F. Bohlmann and G. Haffer, *Chem. Ber.*, **102**, 4017 (1969); (c) T. Durst and K.-C. Tin, *Tetrahedron Lett.*, 2369 (1970); (d) D. F. Tavares, R. E. Estep, and M. Blezard, *ibid.*, 2373 (1970).

(3) (a) W. E. Truce and L. W. Christensen, *Tetrahedron*, **25**, 181 (1969); (b) W. E. Truce and D. J. Vrencur, *Can. J. Chem.*, **47**, 860 (1969).

(4) W. E. Truce and L. W. Christensen, *Tetrahedron Lett.*, 3075 (1969).

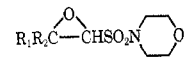
(5) F. G. Bordwell and B. B. Jarvis, *J. Org. Chem.*, **33**, 1182 (1968).

(6) F. G. Bordwell and G. D. Cooper, *J. Amer. Chem. Soc.*, **73**, 5184 (1951).

(7) W. E. Truce, T. C. Klingler, J. E. Parr, H. Feuer, and D. K. Wu, *J. Org. Chem.*, **34**, 3104 (1969).

TABLE I

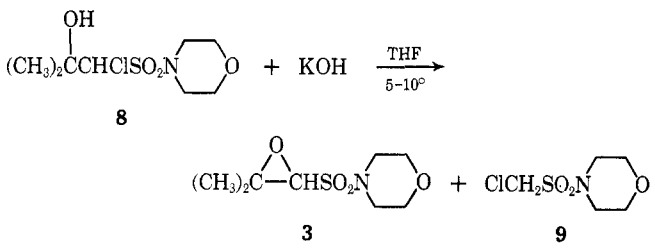
α,β-EPOXYSULFONAMIDES



| No. | Substituents | Mp, °C | Yield,[a] % | Calcd, % C | Calcd, % H | Calcd, % S | Found, % C | Found, % H | Found, % S |
|---|---|---|---|---|---|---|---|---|---|
| 3 | $R_1 = CH_3$ $R_2 = CH_3$ | 67–68 | 75 | 43.48 | 6.84 | 14.51 | 43.20 | 6.90 | 14.49 |
| 4 | $R_1$ = Ph; $R_2$ = Ph | 144–145 | 57[b] | 62.68 | 5.52 | 9.29 | 62.41 | 5.60 | 9.16 |
| 5 | $R_1$, $R_2 = (CH_2)_5$ | 86.5–88 | 66 | 50.26 | 7.30 | 12.25 | 50.55 | 7.53 | 12.06 |

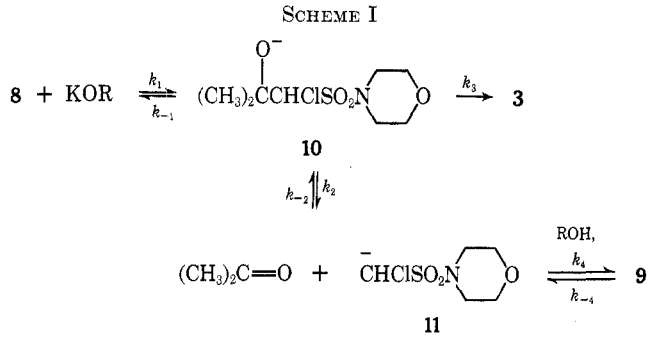
[a] Isolated, purified material, yield not optimized. [b] *Anal.* Calcd for N: 4.06. Found: 3.94.

to warm from −75° to room temperature before hydrolyzing and work-up does not result in epoxide formation. Apparently, when lithium is the cation in the intermediate species **7**, the nucleophilicity of the alkoxide is diminished to such an extent that the displacement will not occur. When potassium is then substituted as cation by interaction of **1** with *tert*-BuOK, the displacement occurs readily. Analogous cation effects in condensations and displacements have been reported previously.[8] In addition to the nature of the cation, it has been found that even the nature of the base itself is crucial for the formation of epoxide. For example, when potassium hydroxide is substituted for potassium *tert*-butoxide, the yield of **3** is greatly diminished (20%) and a large amount (80%) of chloromethylsulfonmorpholide **9** is isolated. Similar results



involving the nature of the base employed have been reported by Bohlmann and Haffer[2] for β-hydroxy-α-chlorosulfones. These results may be rationalized by noting ramifications of the mechanism proposed in Scheme I. Assuming epoxide formation is irreversible,

SCHEME I



*i.e.*, **10** → **3**, then the protonation of **11** is more complete with water as the conjugate acid of the base used (KOH) than with *tert*-butyl alcohol acting as the conjugate acid of the base *tert*-BuOK. Hence, epoxide formation predominates with *tert*-BuOK while fragmentation prodominates when KOH is utilized.

Considering the ease of formation of the precursory β-hydroxy-α-chlorosulfonamides and the facile nature of the ring closure, a useful method is at hand for the preparation of α,β-epoxysulfonic acid derivatives.

(8) E. M. Kaiser and C. R. Hauser, *J. Amer. Chem. Soc.*, **89**, 4566 (1967).

### Experimental Section[9]

**General Procedure for Epoxide Formation from β-Hydroxy-α-Chlorosulfonamides.**—To 0.01 mol of the 1-chloro-2-hydroxysulfonamide in 20 ml of freshly dried THF under $N_2$ at 0° was added *tert*-BuOK (0.01 mol) in 15–20 ml of THF. The addition was carried out at such a rate as to maintain the temperature below 15°. After being stirred for 10 min, 100 ml of 3% aqueous $NH_4Cl$ was added and the resultant solution extracted with five 40-ml portions of $CHCl_3$. The chloroform extracts were dried over $Na_2SO_4$ and then evaporated *in vacuo*, yielding a colorless oil. This oil was taken up in 90% ethanol and cooled, and the resultant solid recrystallized from ethanol to afford pure product.

**Epoxide Formation from 1-Chloro-2-hydroxy-2-methylpropanesulfonmorpholide.**—1-Chloro-2-hydroxy-2-methylpropanesulfonmorpholide (0.90 g, 3.5 mmol) and potassium *tert*-butoxide (0.393 g, 3.5 mmol) afforded 0.58 g (75%) of α,α-dimethyl-β-sulfonmorpholylethylene oxide: mp 67–68°; nmr δ 1.45 (s, 3), 1.70 (s, 3), 3.40 (m, 4), 3.76 (m, 5).

*Anal.* Calcd for $C_8H_{15}NO_4S$: C, 43.48; H, 6.84; S, 14.51. Found: C, 43.20; H, 6.90; S, 14.49.

**Epoxide Formation from 1-Chloro-2-hydroxy-2,2-diphenylethanesulfonmorpholide.**—1-Chloro-2-hydroxy-2,2-diphenylethanesulfonmorpholide (1.30 g, 3.5 mmol) and potassium *tert*-butoxide (0.393 g, 3.5 mmol) yielded 0.69 g (57%) of α,α-diphenyl-β-sulfonmorpholylethylene oxide: mp 144–145°; nmr δ 3.20 (m, 4), 3.60 (m, 4), 4.35 (s, 1), 7.40 (m, 10).

*Anal.* Calcd for $C_{18}H_{19}NO_4S$: C, 62.68; H, 5.52; N, 4.06; S, 9.29. Found: C, 62.41; H, 5.60; N, 3.94; S, 9.16.

**Epoxide Formation from 1-Chloro-1-(1-hydroxycyclohexyl)-methanesulfonmorpholide.**—1-Chloro-1-(1-hydroxycyclohexyl)-methanesulfonmorpholide (1.20 g, 3.41 mmol) and potassium *tert*-butoxide (0.382 g, 3.41 mmol) gave 0.56 g (66%) of the spiral epoxide **5**, mp 86.5–88°. The nmr of the crude reaction mixture also indicated that some fragmentation occurred to afford cyclohexanone and chloromethylsulfonmorpholide: δ 4.51 ($ClCH_2$); nmr δ 1.80 (m, 10), 3.40 (m, 4), 3.70 (m, 5).

*Anal.* Calcd for $C_{11}H_{19}NO_4S$: C, 50.26; H, 7.30; N, 5.36; S, 12.25. Found: C, 50.55; H, 7.53; N, 5.57; S, 12.06.

**Attempted Formation of α,α-Dimethyl-β-sulfonmorpholylethylene Oxide Using Potassium Hydroxide.**—To 1-Chloro-2-hydroxy-2-methylpropanesulfonmorpholide (1.00 g, 3.88 mmol) in 25 ml of THF at 0° under $N_2$ was added powdered potassium hydroxide (0.244 g, 4.0 mmol). After being stirred for 15 min at 15°, 100 ml of 3% aqueous $NH_4Cl$ was added and the resulting mixture extracted with chloroform. The chloroform extracts were dried over $NaSO_4$ and then evaporated *in vacuo* affording a light yellow semisolid, the nmr of which indicated a 20% yield of epoxide and an 80% yield of chloromethylsulfonmorpholide as determined from the signals at δ 4.51 ($ClCH_2$) and 1.50, 1.70 [$(CH_3)_2CO$-C]. *No* starting 1-chloro-2-hydroxysulfonamide could be detected in the nmr spectrum of this crude reaction material. Separation *via* column chromatography using silica gel as adsorbent and dichloromethane as eluent afforded 0.65 g (75%) of **3** and 0.13 g (17%) of **9**.

(9) All melting points are uncorrected. The nmr spectra were obtained in $CDCl_3$ using a Varian A-60 spectrometer with TMS = 0. Microanalyses and molecular weight determinations were performed by Dr. C. S. Yeh and staff. *tert*-BuOK was purchased from MSA Corp. and purified by sublimation. Reagent grade THF was distilled from $LiAlH_4$ prior to use. The α-chloro-β-hydroxysulfonamides were prepared *via* a previously reported procedure.[4]

**Registry No.**—**3**, 30345-08-5; **4**, 30345-09-6; **5**, 30345-10-9.

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## A Novel Synthesis of β-Keto Sulfides

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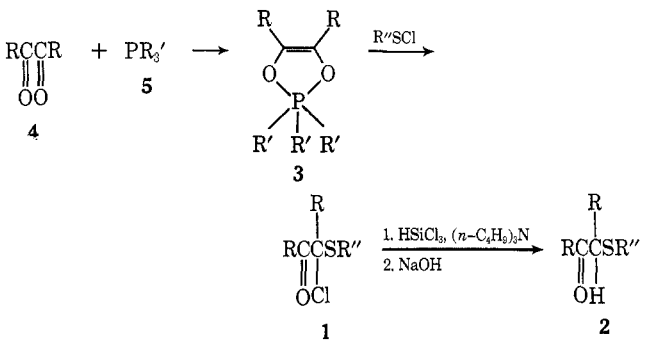
*Received December 31, 1970*

The general utility of β-keto sulfides (and their corresponding sulfoxide derivatives) is well documented.[2] These sulfides are most commonly prepared by the action of mercaptides ($RS^-$) on α-halo ketones,[3a] by reacting sulfenyl halides with ketones[2a] and by the decomposition of dialkylphenacylsulfonium salts with base.[3b] In addition, a number of 3-thianones have recently been prepared *via* a novel intramolecular cyclization reaction.[3c] None of the methods is widely versatile, however, since yields are often low and isomeric products and/or intermediates are encountered. We wish to report a useful new synthesis of β-keto sulfides from simple starting materials. The reactions employed proceed cleanly and in high yield.

The trichlorosilane–tri-*n*-butylamine system[4] reduces α-chloro-β-keto sulfides[5] **1** to β-keto sulfides **2** in nearly quantitative yield. The chloro keto sulfides **1** are




easily prepared[5] by the action of sulfenyl chlorides on substituted 1,3,2-dioxaphospholenes **3**. In addition, the reduction of chloro keto sulfides **1** may be carried out *in situ* from α-diketones **4** and trimethyl phosphite **5** in overall yields of 60–80%. The results are summarized in Table I.

TABLE I

| No. | R | R″ | Mp or bp (mm), °C | Yield, % from **1** (from **4** + **5**) | Nmr data, τ | Calcd, % C | Calcd, % H | Calcd, % S | Found, % C | Found, % H | Found, % S |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **2a** | $C_6H_5$ | $C_6H_4$-*p*-$CH_3$ | 94–96 | 98 (80) | 1.80–3.10 (14 H, m), 4.12 (H, s), 7.73 (3 H, s) | 79.21 | 5.70 | 10.07 | 79.16 | 5.72 | 9.98 |
| **2b** | $C_6H_5$ | $CH_2C_6H_5$ | 70–72 | (60) | 2.10–2.80 (15 H, m), 4.62 (H, s), 6.33 (2 H, AB, $J$ = 14 Hz) | 79.21 | 5.70 | 10.07 | 79.02 | 5.75 | 9.97 |
| **2c** | $C_6H_5$ | $CH_2CH_3$ | 78–80 | (62) | 1.80–2.90 (10 H, m), 4.37 (H, s), 7.50 (2 H, split AB, $J$ = 7 Hz), 8.83 (3 H, t, $J$ = 7 Hz) | 74.96 | 6.29 | 12.51 | 74.85 | 6.33 | 12.43 |
| **2d** | $CH_3$ | $C_6H_5$ | 78–80 (0.003) | 80 (61) | 2.30–2.85 (5 H, m), 6.29 (H, q, $J$ = 7 Hz), 7.80 (3 H, s), 8.63 (3 H, d, $J$ = 7 Hz) | | | 17.79 | | | 17.85 |
| **2e** | $CH_3$ | $CH_2CH_3$ | Dec | | | | | | | | |

### Experimental Section

**Reaction of α-Benzoyl-α-chlorobenzyl *p*-Tolyl Sulfide (1a) with Trichlorosilane and Tri-*n*-butylamine.**—In a 50-ml flask, fitted with a condenser carrying a drying tube and a dropping funnel, was dissolved α-benzoyl-α-chlorobenzyl *p*-tolyl sulfide (1) (0.70 g, 0.02 mol) in dry dimethoxyethane (10 ml). Tri-*n*-butylamine (0.37 g, 0.02 mol) was added, followed by trichlorosilane (0.36 g, 0.026 mol). The reaction mixture was refluxed for 2–3 hr. At the end of the reflux period, it was cooled and poured into a cold solution of 2 *N* sodium hydroxide[6] with stirring. The sodium hydroxide solution was extracted with several portions of methylene chloride. The methylene chloride extracts were combined and washed successively with water, dilute acid, and then water, and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residual solid recrystal-

(1) NRCC scholarship recipient, 1967–1970.

(2) (a) C. Rappe, "Mechanisms of Reactions of Sulfur Compounds," Vol. 4, IntraScience Research Foundation, 1969, p 95. (b) M. C. Caserio, W. Lauer, and T. Novinson, *J. Amer. Chem. Soc.*, **92**, 6082 (1970); G. A. Russell and G. Hamprecht, *J. Org. Chem.*, **35**, 3007 (1970), and references cited therein; G. A. Russell and E. T. Sabourine, *ibid.*, **34**, 2336 (1969).

(3) (a) T. C. Whitner and E. E. Reid, *J. Amer. Chem. Soc.*, **43**, 638 (1921); L. M. Long, *ibid.*, **68**, 2159 (1946). (b) H. Böhme and W. Krause, *Chem. Ber.*, **82**, 426 (1949). (c) P. T. Lansbury, E. J. Nienhouse, D. J. Scharf, and F. R. Hilfiker, *J. Amer. Chem. Soc.*, **92**, 5649 (1970).

(4) These reagents have been used to reduce a number of functionalities: see T. H. Chan, J. P. Montillier, W. F. Van Horn, and D. N. Harpp, *ibid.*, **92**, 7224 (1970); R. A. Benkeser, K. M. Foley, J. M. Gaul, and G. S. Li, *ibid.*, **92**, 3232 (1970); R. A. Benkeser and W. E. Smith, *ibid.*, **90**, 5307 (1968).

(5) D. N. Harpp and P. Mathiaparanam, *Tetrahedron Lett.*, 2089 (1970). In addition, α-chloro-β-keto sulfides of the type RCO(R′)C(Cl)SR″ have been prepared; see F. Weygand, H. J. Bestmann, and H. Fritzsche, *Chem. Ber.*, **93**, 2340 (1960), and references cited therein.

(6) Alkaline conditions were maintained during work-up in order to eliminate any side reactions arising from the hydrolysis of the following possible intermediate, $RC(OSiCl_3)=CR(SR'')$. The trichlorosilyl anion may well be involved; see R. A. Benkeser, K. M. Foley, J. B. Grutzner, and W. E. Smith, *J. Amer. Chem. Soc.*, **92**, 697 (1970), and S. C. Bernstein, *ibid.*, **92**, 699 (1970). At present, however, it is uncertain as to the exact mechanism of this reaction.