Reactions of Bis-alkylsulfonylmethanes and Their Halogen-substituted Derivatives[*]

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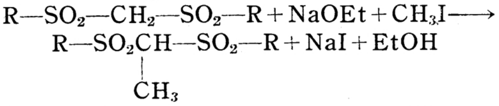
Bis-alkylsulfonylmethane is a fairly interesting compound in many respects.[1] Its central methylene group is active like that of dialkyl malonate and behaves quite similarly. For example, methyl iodide reacts with sodium salt of bis-alkylsulfonylmethane according to the following equation.[1,2]



$$R—SO_2—CH_2—SO_2—R + NaOEt + CH_3I \longrightarrow R—SO_2\underset{\displaystyle CH_3}{\underset{|}{CH}}—SO_2—R + NaI + EtOH$$

This active methylene group readily undergoes electrophilic substitution. A few typical reactions of this type are as follows:

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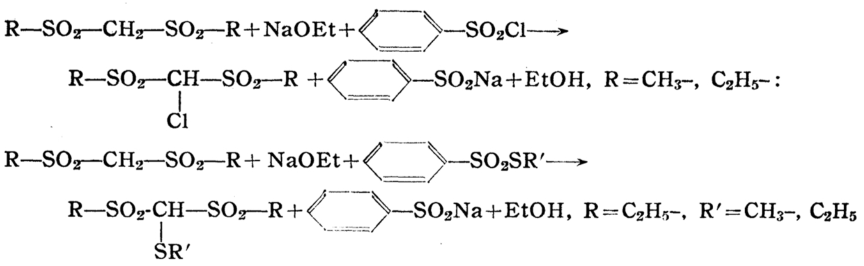
[*] A part of this study was made at the Department of Chemistry, University of Kansas, Lawrence, Kansas, U.S.A.

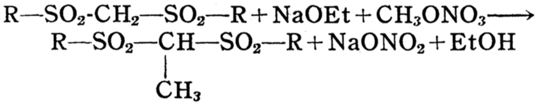
[1] C.M. Suter, "The Organic Chemistry of Sulfur", pp. 739

[2] (a) E. Fromm, *Ann.*, **253**, 141 (1889). E. Fromm et al., ibid., **394** 344 (1912).



The former reaction presumably takes place by the attack of chlorine cation, while the latter does by that of SR′. However, no similar reaction was observed between ethyl benzenesulfonate and bis-alkylsulfonylmethane. This mixture eventually did not react under the same condition as for the sulfur analog.

A reaction was carried out between sodium salt of bis-alkylsulfonylmethane and methyl nitrate under the speculation that it might give bis-alkylsulfonyl-methoxymethane. However, the resulting compound was found to be bis-alkylsulfonyl-methylmethane; namely, it would be a simple nucleophilic substitution.



$$\mathrm{R{-}SO_2{-}CH_2{-}SO_2{-}R + NaOEt + CH_3ONO_3 \longrightarrow R{-}SO_2{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}SO_2{-}R + NaONO_2 + EtOH}$$

Bis-alkylsulfonylmethane is readily halogenated and forms dihalides.[1,2,3] Both dihalide and monohalide of bis-alkylsulfonylmethane show interesting chemical behaviour. Their halogens are easily replaced by hydrogen giving original bis-alkylsulfonylmethane when attacked by nucleophilic reagents. Bis-alkylsulfonyl-dibromomethane reacts with potassium iodide liberating iodine,[2b] while it reacts with thiophenol giving diphenyldisulfide.[1a] Aqueous ammonia, sodium acetate and potassium thiocyanate also replace bromine by hydrogen. These reactions with bis-alkylsulfonyldibromomethane can be explained when one assumes that it gives a bromocation which readily oxidizes nucleophilic reagents. This assumption is probably valid, because halogens attached to the central methylene group having two adjacent strong electron-attractive sulfonyl groups, do not readily split as halogen anions but do so as cations rather easily.

In this investigation, a few more similar reactions were observed. Bis-ethylsulfonylchloromethane gave bis-ethylsulfonylmethane in the reaction with sodium methylate. Sodium methylate converted bis-alkylsulfonyldichloromethane also to its original bis-alkylsulfonylmethane. Aluminum ethylate caused practically the same reaction with bis-methylsulfonydibromomethane.

A somewhat peculiar reaction of bis-ethylsulfonyldibromomethane was one with silver nitrate in methanol. The reaction took place almost spontaneously, one bromine being lost, and gave bis-ethylsulfonylbromomethane, which did not undergo any further reaction with excess silver nitrate. On the other hand, its chloro-analog, bis-ethylsulfonyldichloromethane, reacted very little, even though it was boiled for ten hours with silver nitrate in ethanol. The very much higher reactivity of the dibromo compound over the dichloro-analog can not be ascribed only to the difference in the polarizability of the relevant bond. Moreover, the cleavage of bromine as anion would be greatly suppressed by the inductive effect of the two strongly electron-attractiing sulfonyl groups. The failure of explanation by the electrical effect led us to seek the alternative one by the steric effect. As was reported previously[4], the steric requirement of the sulfonylmethyl group is of similar bulkiness to that of the neopentyl group. According to the current concept of "Strained Homomorph" by H. C. Brown[5], di-(*tert*-butyl)-methane is sterically strained by ca. 5 kcal.; therefore, its 'Strained Homomorph', bis-alkylsulfonylmethane should also be sterically strained by as much as about 5 kcal. When one bromine is substituted for its methylene, the resulting monobromo-compound will have more strain, but the inductive effect of the two strong electron-attractive sulfonyl groups might still overwhelm the steric strain energy, thus rendering the net result the retardation of reactivity. However, when another bromine is introduced, the steric strain of the resulting bis-alkylsulfonyldibromomethane would suddenly jump up to such an extent that the second bromine atom would no longer be held stably at the methylene carbon, in spite of the strong inductive effect of three other

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(b) R.E. Stutz and R.L. Shriner, *J. Am. Chem. Soc.*, **55**, 1242 (1933).
R.L. Shriner et al., ibid., **52**, 2068 (1930).

3) D.T. Gibson, *J. Chem. Soc.*, **1931**, 2637.

4) S. Oae, *Waseda Applied Chem. Bull.*, **21**, No. 1, 7 (1952): ibid., No. 2, 8 (1953).

5) H.C. Brown, *J. Am. Chem. Soc.*, **75**, 1, (1953).

electron-attractive substituents attached to it. Since the chlorine atom is smaller than bromine, even the second chlorine atom might possibly be held with quite enough stability at the methylene carbon, thus showing its inertness in the reaction with silver nitrate.

The reaction of bis-alkylsulfonyldibromomethane with aniline and with toluene were investigated under the speculation that it might be used as a mild brominating agent. However, aniline did not react readily while toluene did, giving benzyl bromide in the presence of a small amount of benzoyl peroxide.

Experimental

Bis-ethylsulfonylmethylmercaptomethane and Bis-ethylsulfonylethylmercaptomethane.—1 g. of methyl *p*-toluenethiosulfonate of m.p. 53–4°, which was prepared by the reaction of methyl iodide upon sodium *p*-toluenethiosulfonate, was reacted with 1 g. of bis-ethylsulfonylmethane in 15 ml. of ethanol dissolving 0.1 g. of metalic sodium. The reaction mixtur was boiled on a water bath for seven hours and then was kept at room temperature overnight. After removing ethanol and allowing the residue to soak in hydrochloric acid until it became acidic, colorless crystalline needles were formed which were collected and recrystalized from ethanol-petroleum ether. 0.7 g. of bis-ethylsulfonyl-methylmercaptomethane of m.p. 119–20° was thus obtained in 57% yield. (Found: S, 39.0. Calcd. for $C_6H_{14}S_3O_4$: S, 39.2%).

Bis-ethylsulfonyl-ethylmercaptomethane of m.p. 103–4° was obtained in 62% yield, starting from ethyl *p*-toluenethiosulfonate of m.p. 50–3° with bis-ethylsulfonylmethane as in the previous case and then recrystallization was performed from benzene-petroleum ether. (Found: S. 36.6; Calcd. for $C_7H_{16}S_3O_4$: S, 36.9%).

The Reaction between Bis-methylsulfonylmethane and Ethyl *p*-toluenesulfonate.—0.5 g. of bis-methylsulfonylmethane was dissolved in 10 ml. of ethanol which dissolved 0.05 g. of metallic sodium. Into this solution, 0.6 g. of freshly prepared ethyl *p*-toluenesulfonate of m.p. 29–30° was added and the whole mixture was boiled on a water bath for an hour. After treating the mixture similarly to the case of thio-analog, only the original substances were isolated. Longer heating was found not to be effective in bringing the reaction any further.

The Reaction between Bis-alkylsulfonylmethane and Methyl Nitrate.—1 g. of bis-methylsulfonylmethane was dissolved in 15 ml. of methanol which dissolved 0.05 g. of metallic sodium. Into this solution 0.5 g. of methyl nitrate was added and the mixture was boiled on a water bath for an hour and a half; then crystals formed. These crystals were collected and were found to be sodium nitrate which was identified by the appearance of blue-violet color when treated with a mixture of diphenylamine and sulfuric acid. The residue was diluted with water and the crystals precipitated were collected. Well-dried crystals were recrystallized from benzene and 0.7 g. of colorless crystals of m.p. 120–122° were obtained. This compound was found to be identical to bis-methylsulfonylmethane of m.p. 124° which was authentically prepared from bis-methylsulfonylmethane and methyl iodide. 0.65 g. of bis-ethylsulfonylmethane and 0.25 g. of methyl nitrate were dissolved in 10 ml. of methanol which contained 0.25 g. of potassium hydroxide, and the mixture was treated as in the previous case, and then bis-ethylsulfonyl-methylmethane of m.p. 75° was obtained. This was identified as bis-ethylsulfonylmethylmethane by the mixed melting point with the authentic sample prepared from bis-ethylsulfonylmethane and methyl iodide.

The Reaction of Sodium Methylate upon Bis-ethylsulfonyldibromomethane.—4 g. of bis-ethylsulfonyl-dibromomethane was added in 40 ml. of methanol which dissolved 0.65 g. of metallic sodium and the whole mixture was boiled for an hour, and then methanol was removed. The residue was diluted with water and the crystals formed were washed with ether, then 2 g. of bis-ethylsulfonylmethane of m.p. 102–3° were obtained. Sodium bromide was obtained from the mother liquor.

The Reaction of Sodium Ethylate upon Bis-methylsulfonyl-dibromomethane.—0.5 g. of bis-methylsulfonyl-dibromomethane was reacted in 5 ml. of ethanol with sodium ethylate made from 0.08 g. of metallic sodium, and then 0.2 g. of bis-methylsulfonylmethane were obtained.

The Reaction of Aluminum Ethylate upon Bis-methylsulfonyl-dibromomethane.—1 g. of bis-methylsulfonyl-dibromomethane was mixed with 0.5 g. of freshly prepared aluminum ethylate, the mixture was sealed in a tube, and the tube was heated at 200° for twenty minutes. After the tube was cooled, the contents were poured into water and then 0.3 g. of crystal melting at 140–45° was obtained. This was identical with bis-methylsulfonylmethane.

The Reaction between Bis-ethylsulfonyl-dibromomethane and Silver Nitrate.—When 1 g. of bis-ethylsulfonyl-dibromomethane was placed into 50 ml. of methanol dissolving 0.5 g. of silver nitrate, the whole solution became milky white and the reaction was over in ten minutes. Then it was further heated up to the boiling point and then was cooled. The silver bromide which formed was filtered off and methanol was removed, and then crystals appeared. These crystals were recrystallized and 0.5 g. of colorless compound of m.p. 121° was obtained. This was found to be monobromo compound. The reaction with large excess of silver nitrate also gave the same compound, though it was heated for a longer period. (Found: Br, 30.0; Calcd. for $C_5H_{11}O_4Br$: Br, 30.4%).

When 0.5 g. of this compound was reacted with 0.3 g. of bromine, the dibromo compound of m.p. 131° was obtained almost quantitatively.

The Reaction between Bis-ethylsulfonyl-dichloromethane and Silver Nitrate.—0.5 g. of bis-ethylsulfonyl-dichloromethane and 0.35 g. of silver nitrate were dissolved in 50 ml. of methanol and the solution was boiled for ten hours, but the solution did not become turbid and the starting material was recovered.

The Reaction between Bis-ethylsulfonyl-dibromomethane and Aniline.—1.5 g. of bis-ethylsulfonyl-dibromomethane and 0.5 g. of aniline were dissolved in 40 ml. of benzene and the solution was boiled for 30 minutes. A small portion of crystal was observed at the end of thirty minutes. Heating was continued for additional four hours and benzene was removed, but no crystalline substance was successfully obtained after a serious attempt.

The same amounts of the starting materials were heated in 50% acetic acid for three hours but only the starting materials were isolated.

The Reaction of Bis-ethylsulfonyl-dibromomethane upon Toluene.—5 g. of bis-ethylsulfonyl-dibromomethane was added to 10 ml. of toluene which dissolved 1 g. of benzoyl peroxide and the whole solution was boiled for five hours. Gradually the solution became lachrymatory. After cooling at the end of five hours, a small portion of benzoic acid of m.p. 120–2° formed in the solution. The remaining oil was distilled in vacuo and 1.5 g. of an oil was obtained which boiled at 70–80°/10 mm. This oil was found to be benzyl bromide which was identified by leading it to S-benzylthiouronium bromide.

Summary

Bis-alkylsulfonylmethane did react with alkyl *p*-toluenethiosulfonate giving bis-alkylsulfonyl-alkylmercaptomethane. Bis-alkylsulfonyl-halogenomethane was found to react with metal alkoxide giving original bis-alkylsulfonylmethane. It was also found that bis-alkylsulfonyl-dibromomethane readily reacts with silver nitrate giving the mono-bromo-compound while its dichloro-analog resists in the same condition.

The mechanisms of these reactions were discussed.

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