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# Alkylation of Sodium Dithionite*1

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Reaction between sodium dithionite and triethyloxonium fluoborate under nitrogen yielded an unstable oil capable of absorbing oxygen. When it was washed and distilled under reduced pressure, ethyl ethanesulfinate was obtained. The reaction between sodium dithionite and alkyl iodides in water or in DMSO yielded dialkyl sulfone. The reaction between sodium ethanesulfinate and triethyloxonium fluoborate in dichloromethane yielded an oily mixture which was 89% ethyl ethanesulfinate and 11% diethyl sulfone. The reaction of alkyl iodides with an excess of sodium dithionite yielded, besides a sulfone, sodium alkanesulfonate, not sodium alkanesulfinate. Mechanisms of these reactions were discussed.

Sodium dithionite (sodium hydrosulfite) is a powerful reducing agent, and its aqueous solution reduces oxygen efficiently at room temperature. Though it is a readily available compound, its ester has not been reported in literature. Since dithionite anion is an ambident anion like sulfinate anion, alkylation of sodium dithionite may result in the formation of both *S*-alkylated and *O*-alkylated products. Therefore, alkylation of sodium dithionite has been investigated by use of several alkylating agents in various solvents, and results will be described in this paper.

## Experimental

**Reaction between Sodium Dithionite and Triethyloxonium Fluoborate.** Nitrogen was bubbled through 40 m*l* of dichloromethane, and then 2.204 g (0.0127 mol) of anhydrous sodium dithionite was suspended in the dichloromethane. Under nitrogen atmosphere 4.784 g (0.0252 mol) of triethyloxonium fluoborate was added to the suspension, and the mixture was stirred for 4.5 hr at room temperature. Inorganic salts were filtered, and the filtrate was washed with 100 m*l* of water and dried over anhydrous magnesium sulfate. Dichloromethane was removed by distillation, and ethyl ethanesulfinate was obtained by distillation of the residue at 66°C/30 mmHg. The yield was 0.284 g (0.18 mol per mol $Na_2S_2O_4$ initially present and 0.42 mol per mol $Na_2S_2O_4$ consumed; see below). It was identified by comparison of its infrared and nuclear magnetic resonance spectra with those of the authentic sample.

As a separate experiment a similar mixture of sodium dithionite and triethyloxonium fluoborate was stirred under the same conditions for 4.5 hr, and the inorganic residue was analyzed for sodium dithionite. It was found that 56% of sodium dithionite remained unreacted.

**Reaction between Sodium Dithionite and Methyl Iodide.** In 25 m*l* of deaerated water 5.046 g (0.0284 mol) of sodium dithionite and 12 g of methyl iodide (0.080 mol) were dissolved, and the mixture was stirred and refluxed (40—50°C) for 105 min under nitrogen atmosphere. The organic components were extracted with dichloromethane, and the dichloromethane solution was dried over magnesium sulfate. Evaporation of the solvent yielded crystals of dimethyl sulfone; 0.24 g (9%), mp 105.5—106.0°C.

**Reaction between Sodium Ethanesulfinate and Triethyloxonium Fluoborate.** Pure sodium ethanesulfinate was prepared by alkaline hydrolysis of ethyl ethanesulfinate, which was synthesized from ethanesulfinyl chloride and ethanol.[1] It was dried in vacuum at 120°C.

To 3.130 g (0.0270 mol) of dried sodium ethanesulfinate, 30 m*l* of a dichloromethane solution containing 5.48 g (0.0290 mol) of triethyloxonium fluoborate was added, and the mixture was stirred for 5 hr at room temperature. Inorganic solids were filtered, and the filtrate was washed with water and then dried over magnesium sulfate. Evaporation of dichloromethane yielded an oil which was identified by its infrared spectrum to be a mixture of ethyl ethanesulfinate and diethyl sulfone. The yield was 2.35 g (0.70 mol per mol of sodium ethanesulfinate). The amounts of the two components were determined by use of the absorption at 890 $cm^{-1}$ for the ester ($\varepsilon=222$) and the absorption at 1320 $cm^{-1}$ for the sulfone ($\varepsilon=748$). The molar ratio of the ester and the sulfone was found to be 88.7 : 11.3.

## Results and Discussion

When sodium dithionite and triethyloxonium fluoborate were stirred in dichloromethane at room temperature for 4.5 hr and then the solvent was removed, an oily residue was obtained, which was capable of absorbing oxygen. Attempts to crystallize the residue failed, and distillation under reduced

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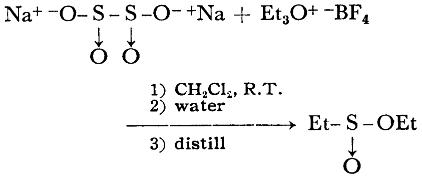
*1 Part XVIII of Organic Sulfur Compounds.

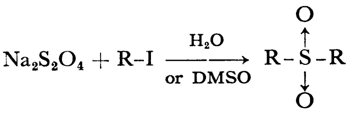
1) E. J. Corey and T. Durst, *J. Amer. Chem. Soc.*, **90**, 5550 (1968); I. B. Douglass, *J. Org. Chem.*, **30**, 634 (1965).

pressure did not yield identifiable products. However, when the oil was washed with water and then distilled under reduced pressure, ethyl ethanesulfinate was obtained in 42% yield (on the basis of the sodium dithionite consumed). Thus, this reaction is regarded as a one-step synthesis of ethyl ethanesulfinate.



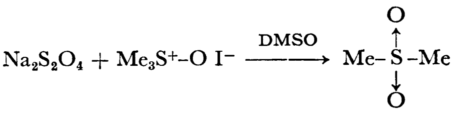
$$\mathrm{Na^+\,{}^-O-\underset{\substack{\downarrow\\ O}}{S}-\underset{\substack{\downarrow\\ O}}{S}-O^-\,{}^+Na + Et_3O^+\,{}^-BF_4} \xrightarrow[\text{3) distill}]{\text{1) CH}_2\text{Cl}_2\text{, R.T.} \quad \text{2) water}} \mathrm{Et-\underset{\substack{\downarrow\\ O}}{S}-OEt}$$

When methyl iodide was refluxed with sodium dithionite in water or in 20% methanol-water or in dimethyl sulfoxide, dimethyl sulfone was the only product. From ethyl iodide diethyl sulfone was obtained under similar conditions. When trimethylsulfoxonium iodide was stirred with sodium dithionite in dimethyl sulfoxide at 60°C, dimethyl sulfone was obtained.



$$\mathrm{Na_2S_2O_4 + R{-}I} \xrightarrow[\text{or DMSO}]{\mathrm{H_2O}} \mathrm{R-\overset{\substack{O\\ \uparrow}}{\underset{\substack{\downarrow\\ O}}{S}}-R}$$

(R = Me or Et)

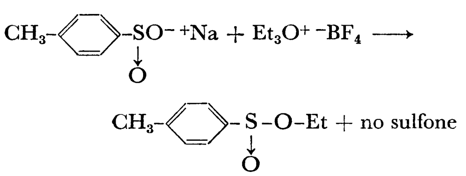


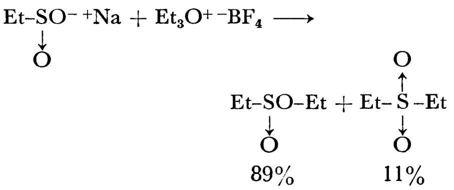
$$\mathrm{Na_2S_2O_4 + Me_3S^+{-}O\ I^-} \xrightarrow{\text{DMSO}} \mathrm{Me-\overset{\substack{O\\ \uparrow}}{\underset{\substack{\downarrow\\ O}}{S}}-Me}$$

The findings that a powerful alkylating agent ($\mathrm{Et_3O^{+-}BF_4}$) can attack oxygen atoms while weaker alkylating agents (RI, $\mathrm{Me_3S^+O\ I^-}$) can react only with sulfur atoms are in line with the results obtained for alkylation of sodium *p*-toluenesulfinate.[2]

It should be mentioned that anhydrous sodium dithionite is extraordinarily insoluble in organic solvents. It is insoluble not only in non-polar organic solvents but also in such polar solvents as acetonitrile, dimethyl sulfoxide, *N,N*-dimethylformamide, hexamethylphosphoramide, nitromethane, acetone and alcohols.

It was previously reported that *O*-alkylation takes place exclusively when sodium *p*-toluenesulfinate was treated with triethyloxonium fluoborate in dichloromethane.[3] However, there have been no reports describing a similar reaction with sodium alkanesulfinate. When sodium ethanesulfinate was stirred with triethyloxonium fluoborate in dichloromethane for 5 hr and then the solvent was evaporated, the residual oil was found to be composed of 89% ethyl ethanesulfinate and 11% diethyl sulfone. This difference in the reactivities of arenesulfinate anion and alkanesulfinate anion may be ascribable to the delocalization of the lone pair on sulfur due to the resonance involving benzene ring in the case of arenesulfinate anion and to the lack of such delocalization in the case of alkanesulfinate anion.

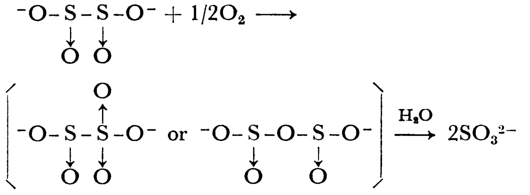




$$\mathrm{Et{-}\underset{\substack{\downarrow\\ O}}{S}O^-\,{}^+Na + Et_3O^+\,{}^-BF_4 \longrightarrow Et{-}\underset{\substack{\downarrow\\ O}}{S}O{-}Et + Et-\overset{\substack{O\\ \uparrow}}{\underset{\substack{\downarrow\\ O}}{S}}-Et}$$

89% 11%

No quantitative determinations have been reported as to the absorption of oxygen by a sodium dithionite solution. When sodium dithionite was dissolved in deaerated water and then a measured amount of oxygen was introduced, it was found that half a mole of oxygen was absorbed per mole of sodium dithionite. The reaction is probably expressed as follows.



$$\mathrm{{}^-O-\underset{\substack{\downarrow\\ O}}{S}-\underset{\substack{\downarrow\\ O}}{S}-O^- + 1/2O_2 \longrightarrow \left[{}^-O-\underset{\substack{\downarrow\\ O}}{S}-\overset{\substack{O\\ \uparrow}}{\underset{\substack{\downarrow\\ O}}{S}}-O^- \ \text{or}\ {}^-O-\underset{\substack{\downarrow\\ O}}{S}-O-\underset{\substack{\downarrow\\ O}}{S}-O^-\right] \xrightarrow{H_2O} 2SO_3^{2-}}$$

When sodium dithionite and triethyloxonium fluoborate were stirred in dichloromethane and then the solvent was evaporated, the oily residue obtained was capable of absorbing oxygen. It is possible that this mixture contained diethyl dithionite, though attempts for its characterization did not succeed.

As for the mechanism of the reaction between sodium dithionite and triethyloxonium fluoborate, various routes are possible such 1) *O*-alkylation twice, 2) *O*-alkylation followed by *S*-alkylation, 3) the reverse of 2), 4) *S*-alkylation twice, *etc.* Since no sulfone was found as a product and diethyl sulfone was a product from the reaction between the triethyloxonium salt and ethanesulfinate anion, the mechanisms involving ethanesulfinate anion as a chief intermediate can be excluded. Since no α-disulfone was found and the hydrolysis of an α-disulfone yields ethanesulfinate anion,[4] the possibility 4) can be excluded. Possibilities 2) and 3) would yield ethyl ethoxysulfinyl sulfone, which does not appear to be capable of absorbing oxygen,

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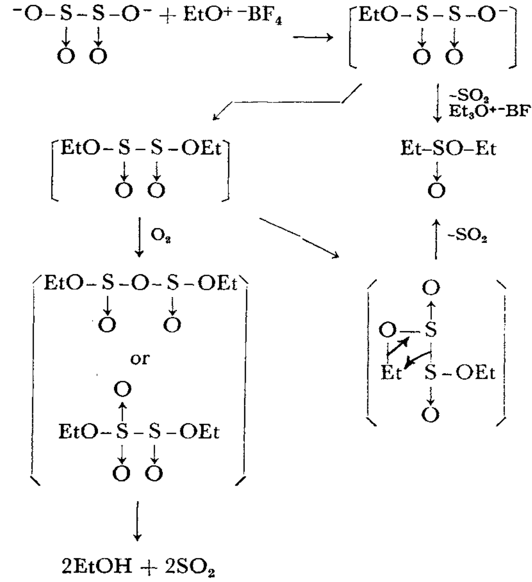
[2] J. S. Meek and J. S. Fowler, *J. Org. Chem.*, **33**, 3422 (1968).

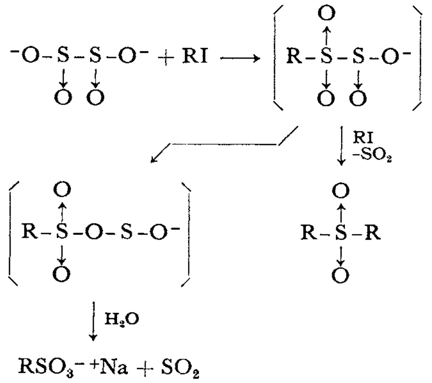
[3] M. Kobayashi, This Bulletin, **39**, 1296 (1966).

[4] P. Allen, Jr., and P. J. Conway, *Can. J. Chem.*, **47**, 873 (1969).

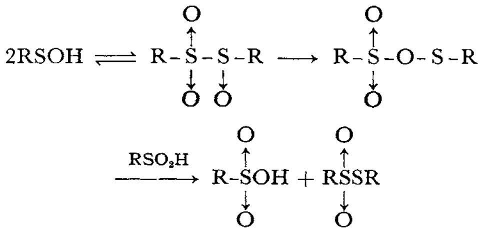
nor to yield ethyl ethanesulfinate upon further reaction. On the basis of various findings and considerations, the following mechanism appears to be most plausible.



The reaction between sodium dithionite and alkyl iodides probably involves alkanesulfonylsulfinate anion as an intermediate. In order to check whether or not an alkanesulfinate anion is formed as an intermediate, 5 mol of sodium dithionite were treated with a mole of ethyl iodide in water under nitrogen. Evaporation of water and extraction with ethanol yielded sodium ethanesulfonate, and no soidum ethanesulfinate. In several experiments with sodium dithionite and alkyl iodides, yields of sulfones were always low and usually less than 9%. The formation of sodium alkanesulfonate and the low yields of sulfones may be explained by the following scheme.



The intermediate alkanesulfonylsulfinate resembles alkyl alkanesulfinyl sulfone studied by Kice and his co-workers, who established that a sulfinylsulfone homolytically decomposes and the combination of the radicals formed yields sulfonyl sulfenyl anhydride.[5]



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5) J. L. Kice and N. E. Pawlowski, *J. Amer. Chem. Soc.*, **86**, 4898 (1964); J. L. Kice, G. Guaraldi and C. G. Venier, *J. Org. Chem.*, **31**, 3561 (1966).