The Reaction of Di-*n*-butyl Sulfoxide and Related Compounds with Elemental Sulfur[1]

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Earlier, we have shown that the reactions of diphenyl sulfoxide, sulfone[2] and dibenzyl analogs[3] with elemental sulfur proceed through different mechanistic routes, and suggested that the different modes of the reactions can be interpreted in terms of the differences in the weakest bonds of the respective compounds. As an extension of the previous works, we now have investigated the reaction of di-*n*-butyl sulfoxide with elemental sulfur; this paper will describe the reaction in detail and will also give a few additional data on similar reactions of di-*n*-butyl sulfide and sulfone.

When the reaction of di-*n*-butyl sulfoxide was carried out, as in the previous experiments with dibenzyl compounds, the evolution of hydrogen sulfide was noticed at above 160°C. The formation of water was also noticed, but not that of sulfur dioxide as in the case of dibenzyl compounds. However, the reactions of di-*n*-butyl compounds appear to be somewhat more sluggish than those of the dibenzyl derivatives. The oily products were separated into pure forms by gas liquid chromatography and thin-layer-chromatography, and were identified by means of their IR spectra. The results are shown, together with those of di-*n*-butyl sulfide and sulfone, in Table 1.

The major organic product in this reaction was di-*n*-butyl sulfide and the amount of the disulfide formed was only one-fifteenth of that of the major product.

$$(n\text{-}C_4H_9)_2SO \xrightarrow[\Delta]{S_8} \underset{\text{15 part}}{n\text{-}(C_4H_9)_2S} + \underset{\text{1 part}}{(n\text{-}C_4H_9)_2S_2} + H_2O + H_2S$$

A tracer experiment between di-*n*-butyl sulfoxide-^{35}S and natural sulfur was carried out. The sulfide formed was oxidized to the sulfone, the ^{35}S activity of which was then counted using a liquid scintilation counter; it was found to retain practically all the ^{35}S activity that di-*n*-butyl sulfoxide originally possessed. That is, the reaction was a clear-cut reductive cleavage of the S–O bond of the sulfoxide to form the sulfide as in the case of diphenyl sulfoxide. It is worthy to note however, that the reductive cleavage of the S–O bond of di-*n*-butyl sulfoxide occurred at a much lower temperature than that of diphenyl sulfoxide.

Two mechanisms are conceivable; one is the reductive cleavage of the sulfoxide bond induced by the sulfur radical formed by the thermal cleavage

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[1] Paper XIII on Sulfoxides.

[2] S. Oae and S. Kawamura, This Bulletin, **36**, 163 (1963).

[3] W. Tagaki, S. Kiso and S. Oae, *ibid.*, **38**, 414 (1965).

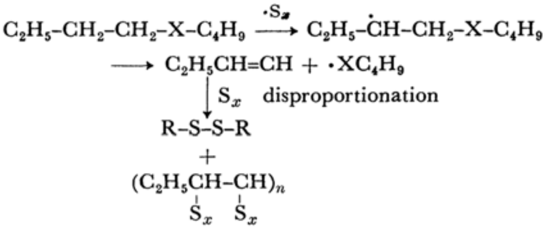
Table 1. Reaction conditions and the yields of the products

Compound $R=n\text{-}C_4H_9$	Reaction temp. °C	Reaction time hr	Weight of the reaction mixture		Yield of the product, mg (%)[a]						
			Compound mg	Sulfur mg	PbS	Oil	RSSR	H_2O	SO_2	Residue	React %
R_2SO	200	8	4712	931	2387 (33.5)	2409[b] (50.3)	+	356 (76)	—	1246[c]	78
R_2S	200	8	2987	646	702 (12.1)	2370[d] (80)	+[e]	—	—	900[f]	*ca.* 20
R_2SO_2	200	9	3566	650	865 (17.9)	105[g] (5.2)	+	—	—	3603[h]	*ca.* 20

a) Percentage yield based on the amount of the starting compound.
b) Mixture of di-*n*-butyl sulfide and disulfide (*ca.* 15 : 1).
c) Mixture of unreacted sulfur and a black solid cake containing carbon, hydrogen and sulfur.
d) Mainly di-*n*-butyl sulfide.
e) Found in the residue.
f) Mixture of sulfur, di-*n*-butyl sulfide, and a tarry substance.
g) Mixture of di-*n*-butyl disulfide and an unidentified compound bearing a carbonyl group.
h) Mixture of sulfur and the unreacted sulfone.

of the sulfur molecule above 160°C,[4] and the other is a nucleophilic reaction between the sulfoxide and sulfur molecule. In so far as the bond force constants of the sulfoxide groups of both diphenyl and di-*n*-butyl sulfoxides are nearly the same, *i.e.*, roughly 6.95×10^{-5} to 7.0×10^{-5} dyn/cm, for both compounds,[5] while the basicity of diphenyl sulfoxide ($pK_a-3.58$)[6] is considered to be substantially smaller than that of di-*n*-butyl sulfoxide since that of dimethyl sulfoxide is know to be pK_a 0.911,[5] the facile cleavage of the sulfoxide over that of di-*n*-butyl sulfoxide seems to favor the latter path, involving the nucleophilic attack of the sulfoxide group on the sulfur molecule, since the relative ease of the reductive cleavage is considered to depend on the strength of the sulfoxide bond. Similar reactions of pyridine *N*-oxides and phenoxanthin sulfoxide with diaryl disulfide apparently proceed through the nucleophilic process.[7]

Under the same conditions, the reactions of both the sulfide and the sulfone were sluggish. However, in all three cases, a small amount of di-*n*-butyl disulfide was formed. The formation of both the disulfide and hydrogen sulfide in all three cases, and that of a black solid containing sulfur (similar to hard rubber) in the case of the sulfoxide, may be explained on the assumption that a simultaneous hydrogen abstraction reaction took place at the α-position of these sulfur groups, as in a free-radical reaction of dialkyl sulfide,[8] (since the reaction would lead to the transient formation of butene-1, which would then further react with sulfur radicals to produce not only the disulfide, but also other sulfur-containing polymeric materials).



$$C_2H_5\text{–}CH_2\text{–}CH_2\text{–}X\text{–}C_4H_9 \xrightarrow{\cdot S_x} C_2H_5\text{–}\dot{C}H\text{–}CH_2\text{–}X\text{–}C_4H_9 \longrightarrow C_2H_5CH{=}CH + \cdot XC_4H_9 \xrightarrow[\text{disproportionation}]{S_x} R\text{–}S\text{–}S\text{–}R + (C_2H_5\underset{S_x}{CH}\text{–}\underset{S_x}{CH})_n$$

Similar reactions of olefin with sulfur are known.[9] The formation of water in the cases of the sulfoxide and the sulfone is probably due to the reduction of an oxygen-containing intermediate by hydrogen sulfide.

Experimental

The Syntheses of the Starting Compounds. Di-*n*-butyl sulfide (bp 93—95°C/35 mmHg) and the sulfone (mp 41.5—42°C) were prepared by known methods,[10] while di-*n*-butyl sulfoxide (bp 120°C/1.2 mmHg) was prepared by our own procedure.[11] ^{35}S-labeled di-*n*-butyl sulfide was prepared from *n*-butyl bromide and ^{35}S-labeled thiourea. The ^{35}S-labeled sulfide was oxidized to the sulfoxide by the usual oxidation.[11] The overall yield of the sulfoxide was 30.6%, based on the amount of thiourea employed. The activity of the

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[4] a) G. W. Ross, *J. Chem. Soc.*, **1958**, 2856; b) L. Bateman, C. G. Moore and M. Porter, *ibid.*, **1958**, 2866.

[5] C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press, N. Y. (1962), Chapter 3.

[6] K. K. Andersen, W. H. Edmonds, J. B. Biasotti and R. A. Strecker, *J. Org. Chem.*, **31**, 2859 (1966).

[7] K. Ikura and Y. Shimano, unpublished works.

[8] E. S. Huyser and R. M. Kellogg, *J. Org. Chem.*, **31**, 3366 (1966).

[9] L. Bateman and C. G. Moore, "Reactions of Sulfur with Olefins," Chapter 20, in "Organic Sulfur Compounds," ed. by N. Kharash, Pergamon Press, New York (1961).

[10] D. T. McAllan, T. V. Cullum, R. A. Dean and F. A. Fidler, *J. Am. Chem. Soc.*, **73**, 3627 (1951).

[11] a) S. Oae, Y. Ohnishi, S. Kozuka and W. Tagaki, This Bulletin, **39**, 364 (1966); b) Y. Ohnishi, unpublished work.

sulfoxide was determined by converting it to the sulfone, which was then subjected to the actual scintilation counting. The activity of the sample: 1790 cpm/mg S.

General Procedure for the Reaction with Elemental Sulfur. The reaction apparatus and the procedure employed were the same as in the previous case with dibenzyl compounds; they have been described elsewhere.[4]

In the case of di-*n*-butyl sulfoxide, oil and water were trapped in a trap cooled by dry ice and acetone. The water was separated first, and then the oil portion was subjected to GLC directly, using a column packed with high-vacuum silicon on celite-535, with a hydrogen stream running through. The sulfide came out first, followed by a small peak of the disulfide. From the peak heights of the two components, the ratio of the yields was estimated to be 15: 1. Both compounds were identified by comparing their GLC properties and IR spectra with those of authentic samples. The disulfide was prepared according to the literature[12]; bp 226°C at 760 mmHg. Di-*n*-butyl sulfide was further oxidized to the sulfone (mp 42°C) by the usual oxidation with hydrogen peroxide in acetic acid. From the black residue (1246 mg) extraction with boiling benzene gave unreacted sulfur (103 mg), leaving a black solid, similar to hard rubber. In the reaction of di-*n*-butyl sulfide with elemental sulfur, unreacted di-*n*-butyl sulfide was distilled into the trap and a small amount of the disulfide was detected by the analysis of the residual tar through GLC. Although the IR spectrum of the tar contained distinct bands at 1540, 1150, and 1180 cm^{-1} that were not found in those of the sulfide and the disulfide, no further isolation of other products was carried out.

The reaction of di-*n*-butyl sulfone under the same conditions was quite slow, and many of the starting materials were found among the residue, while water, the disulfide, and an unidentified liquid were collected in the trap after the usual distillation. The disulfide that came out through the same GLC run at 130°C with a hydrogen stream of 40 cc/min was identified by comparing its IR spectrum with that of the authentic sample. The other component, which came out earlier through the same GLC, had a distinct carbonyl frequency band of 1710 cm^{-1}, but it was not characterized.

Tracer Experiment with ^{35}S-labeled Di-*n*-butyl Sulfoxide. The reaction was carried out with 4.23 g of di-*n*-butyl sulfide-^{35}S (sp. activity: 1790 cpm/mg S) and 0.71 g of sulfur at 200°C. The reaction was stopped after 10 hr of heating, and the sulfide (0.76 g) collected in the trap was oxidized to the sulfone by the use of 5 m*l* of 30% hydrogen peroxide in 20 m*l* of acetic acid. The activity of the sulfone thus obtained in a 90% yield was measured in a toluene solution using POPOP as the scintilator and using Packard TriCarb. The specific activity of the sulfone was found to be 1780 cpm/mg S.

We are grateful to Mr. S. Kawamura of the Radiation Center of Osaka Prefecture, who generously performed the actual counting of the specific activities of our ^{35}S-labeled samples.

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[12] R. E. Stutz and R. L. Shriner, *J. Am. Chem. Soc.*, **55**, 1242 (1933).