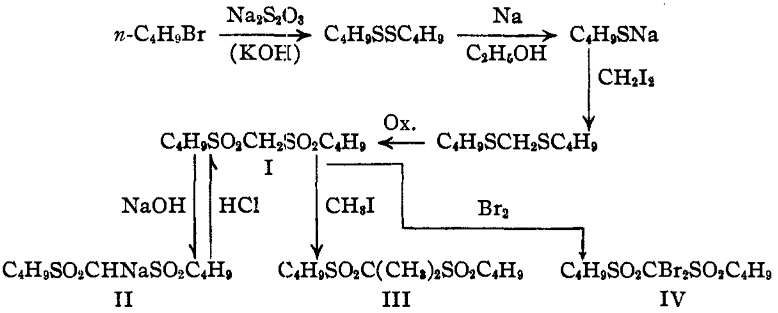
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Preparation and Properties of Methylene Di-*n*-butyl Disulfone

BY R. E. STUTZ AND R. L. SHRINER

Methylene diphenyl disulfone has been found to be easily alkylated and readily soluble in aqueous sodium hydroxide.[1] The activity of the methylene group in this compound was greater than that of a methylene group in 1,3-diketones and appeared to be due to the fact that it is situated between two sulfonyl groups. However, the two phenyl radicals may also have had some activating influence. Hence, it was desirable to study a compound in which the phenyl radicals had been replaced by alkyl groups. The following chart (I) summarizes the preparation and reactions of such a compound, namely, methylene di-*n*-butyl disulfone.

CHART I



Methylene di-*n*-butyl disulfone (I) was found to be soluble in dilute sodium hydroxide solution yielding the salt (II) and upon acidification the original compound (I) was obtained. It was readily alkylated to the disubstituted product III which was alkali insoluble. Bromination produced the bromo derivative IV. The bromine in this compound liberated iodine from potassium iodide solution. These properties show the methylene group to be unusually active. Since the properties of this disulfone parallel those of methylene diphenyl disulfone it seems probable that the methylene group owes its reactivity to the two sulfonyl groups and that the other radicals attached to the sulfur atom have negligible influence. The properties of this disulfone constitute further experimental evidence in favor of the structure of sulfones and their salts previously discussed.[1]

The synthetic procedure outlined in Chart I was unique in that it avoided the preparation of the disagreeable mercaptans. The reaction[2] between *n*-butyl bromide, alcoholic sodium thiosulfate and potassium hydroxide proceeded smoothly to give 44–47% yields of dibutyl disulfide which was

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[1] Shriner, Struck and Jorison, THIS JOURNAL, **52**, 2060 (1930).

[2] Spring and Legros, *Ber.*, **15**, 1938 (1882); Price and Twiss, *J. Chem. Soc.*, **93**, 1395 (1908).

reduced to the sodium mercaptide by sodium and alcohol. The solution of the mercaptide was used directly for the reaction with methylene iodide.

It has also been found that organic disulfides dissolved in toluene or xylene may be cleaved by sodium[3] or sodium-potassium alloy to the metal alkyl or aryl mercaptide which may be readily characterized by condensation with 2,4-dinitrochlorobenzene.[4] The yields of metal mercaptides obtained by direct cleavage were lower than by reduction with sodium and alcohol, but either method now affords a means of preparing various types of mixed thioethers without the necessity of working with the very disagreeable mercaptans. From these thioethers in turn many interesting compounds may be made. The reactions which lead to the methylated sulfone (III) constitute a new method for the synthesis of homologs of sulfonal.

Experimental

Di-*n*-butyl Disulfide.—To 137 g. of *n*-butyl bromide and 500 cc. of alcohol in a 2-liter three-necked flask fitted with a mercury-sealed stirrer was added 300 g. of sodium thiosulfate dissolved in 400 cc. of water and the mixture refluxed for one and one-half hours. Then 140 g. of potassium hydroxide in 300 cc. of water was added and the mixture again heated for half an hour. The disulfide separated as an oil and the alkali sulfate and sulfite salts precipitated. The di-*n*-butyl disulfide after extraction with ether was distilled and collected at 120–123° under 25–30 mm.; yield, 42 g. (47%) of a slightly yellow liquid,[5] b. p. 226° at 760 mm.; d^{20}_{20} 0.944, n^{20}_{D} 1.4926; M_D calcd., 55.38; found, 54.90.

Methylene Di-*n*-butyl Disulfide.—To 50 g. of di-*n*-butyl disulfide in 800 cc. of absolute alcohol, in a 2-liter three-necked flask equipped with a mercury-sealed stirrer and reflux condenser, was added 40 g. of sodium. After the sodium had dissolved, 21 cc. fo water was added to react with the excess sodium ethylate.

The stirrer was started and 77 g. of methylene iodide added slowly (one hour). The mixture was refluxed with stirring for three hours. Three 200-cc. portions of alcohol were distilled from the solution and replaced with water. The product was extracted with ether and distilled: b. p. 133–138° at 30–35 mm. (b. p. 250° at 760 mm.); yield, 44 g. (82%); d^{20}_{20} 0.947; n^{20}_{D} 1.4946; M_D calcd., 59.72; found, M_D, 59.26.

Anal. Calcd. for $C_9H_{20}S_2$: S, 33.35. Found: S, 33.11.

Methylene Di-*n*-butyl Disulfone.—To 27.6 g. of methylene di-*n*-butyl disulfide in 200 cc. of glacial acetic acid, 84 g. of chromium trioxide was added over a period of one and one-half hours. The flask was warmed at first, but later the reaction proceeded smoothly without further heating. After the reaction had stopped the mixture was poured on crushed ice, filtered and purified by recrystallizing twice from water, and once from absolute alcohol; m. p. 95–96°; yield 4.7 g. or 13%. The product readily dissolved in 5% aqueous sodium hydroxide and was precipitated by hydrochloric acid.

Anal. Calcd. for $C_9H_{20}O_4S_2$: S, 25.00. Found: S, 24.69.

A compound described as methylene di-*n*-butyl disulfone with a melting point of 182° has been previously mentioned by Whitner and Reid,[6] who prepared it by oxidizing the disulfide with sodium dichromate and sulfuric acid or with fuming nitric acid. The preparation of the disulfone was repeated using the dichromate oxidation and the prod-

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[3] Lecher, *Ber.*, **48**, 524 (1915); **48**, 1425 (1915); **55**, 577 (1920).

[4] Bost, Turner and Norton, THIS JOURNAL, **54**, 1985 (1932).

[5] Hunter and Sorenson, *ibid.*, **54**, 3366 (1932).

[6] Whitner and Reid, *ibid.*, **43**, 638 (1921).

uct found to melt at 95–96°. An attempted oxidation by means of fuming nitric acid resulted in a violent reaction from which nothing could be isolated. Moreover, Stuffer[7] found the melting point of methylene di-isobutyl disulfone to be 85° and Posner[8] found 138–139° for methylene diamyl disulfone. The melting point for the di-*n*-butyl compound (95–96°) falls between these values as would be expected.

Bromination of Methylene Di-*n*-butyl Disulfone.—To 0.2 g. of methylene di-*n*-butyl disulfone dissolved in 600 cc. of hot water was added 0.5 g. of bromine and the mixture warmed on the steam cone for two hours. The solution was then cooled in ice and the colorless needle-like crystals filtered and recrystallized from absolute alcohol; m. p. 80°, yield, 0.15 g. or 47%.

Anal. Calcd. for $C_9H_{18}O_4S_2Br_2$: Br, 38.59. Found: Br, 38.56.

Alkylation of Methylene Di-*n*-butyl Disulfone.—To a solution of 0.15 g. of sodium in 100 cc. of absolute alcohol was added 0.85 g. of methylene di-*n*-butyl disulfone. Next 1 cc. of methyl iodide was added and the mixture refluxed for 2.25 hours. Fifty cubic centimeters of alcohol was distilled from the flask and the residue poured on crushed ice. The product was filtered by suction and recrystallized from ligroin; colorless needles; m. p. 67–68°; mixed melting point with the original disulfone (m. p. 95–96°), 54–57°; yield, about 0.4 g. or 40%. The product was insoluble in aqueous alkalies.

Anal. Calcd. for $C_{11}H_{24}O_4S_2$: S, 22.55. Found: S, 22.65.

Cleavage of Di-*n*-butyl Disulfide.—The rupture at the sulfur–sulfur linkage in disulfides may also be brought about in the following manner.

A. With Metallic Sodium.—One and twenty-five hundredths grams of metallic sodium was added to 100 cc. of dry xylene contained in a 200-cc. round-bottomed flask equipped with a reflux condenser. Five grams of di-*n*-butyl disulfide was added and the mixture heated on the steam cone for twelve hours. The product was filtered and washed with absolute ether. Following the method suggested by Bost, Turner and Norton[4] the mercaptide was then converted to the 2,4-dinitrophenyl thioether, which was obtained as yellow needles; m. p. 66° (m. p. lit. 66°); yield 6 g. or 42%.

B. With Sodium–Potassium Alloy.—The sodium–potassium alloy was prepared by adding 1.05 g. of potassium and 0.62 g. of sodium to 100 cc. of dry xylene and then heating until alloyed. Five grams (slight excess) of di-*n*-butyl disulfide was then added to the hot liquid alloy and the mixture allowed to stand overnight. To ensure complete reaction with the metal, the mixture was heated for several hours on the steam cone. The mixed mercaptide thus formed was likewise purified and characterized as the 2,4-dinitrophenyl thioether, giving yellow needles; m. p. 66°, yield 6.5 g. or 45%.

Cleavage of Diphenyl Disulfide

A. With Powdered Metallic Sodium.—Five grams of diphenyl disulfide was treated with 1.05 g. of sodium in xylene as above. In this case, however, the metal was first reduced to a powder. The reaction rate was noticeably increased; yellow needles of the 2,4-dinitrophenyl thioether were obtained; m. p. 121° (m. p. recorded, 121°), yield 5.5 g. or 44%.

B. With Sodium–Potassium Alloy.—The alloy was prepared as above. Five grams of diphenyl disulfide, 0.52 g. of sodium and 88 g. of potassium gave a product which when treated with 2,4-dinitrochlorobenzene gave yellow needles; m. p. 121°; yield 7.5 g. or 60%.

Summary

Methylene di-*n*-butyl disulfone has been prepared and found to be soluble in aqueous alkalies, easily brominated and readily alkylated.

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(7) Stuffer, *Ber.*, **23**, 3230 (1890).

(8) Posner, *ibid.*, **36**, 296 (1903).

Sodium or sodium–potassium alloy cleaved alkyl and aryl disulfides to the metal mercaptides.

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The Action of Alkalies on the Monobasic Sugar Acids.[1] I. Conversion of Gluconic to Mannonic and of Galactonic to Talonic Acids by the Action of Barium Hydroxide

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This paper records experiments on the action of barium hydroxide on several monobasic sugar acids. It has been found that epimerization of these acids may be produced by the action of barium hydroxide and that the action of pyridine, quinoline and other tertiary amines is not specific in this process. Thus, *d*-gluconic acid has been converted to *d*-mannonic acid, *d*-mannonic to *d*-gluconic, and *d*-galactonic to *d*-talonic acid. The mannonic and talonic acids have been isolated in the form of their γ-lactones.

The preparation of *d*-mannonic acid by the epimerization of *d*-gluconic acid was discovered by Fischer[2] and recently Nelson and Cretcher[3] have described its preparation from ivory-nut meal.

d-Talonic acid was prepared from *d*-galactonic acid by Fischer,[4] and Cretcher[5] has recently published an improved method.

That barium hydroxide is capable of producing epimeric change is of interest in connection with the general problem of the oxidation of sugars in alkaline solution. Thus in the oxidation of glucose by Fehling's solution[6] and by the Soldaini reagent,[7] mannonic acid or a derivative has been isolated as one product, and gluconic acid has been obtained in the oxidation of mannose.[8] In like manner *d*-talonic acid was found as an oxidation product of galactose in the work of Anderson.[9] Nef[8] and also Anderson[9] explained the formation of the isomeric hexonic acid in the oxidation of a given hexose, as the result of a benzilic acid rearrangement of the 1,2-osone, formed by the oxidation of the 1,2-enediol of the hexose. Jensen and Upson[10] suggested that an alternative explanation is to be

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[1] An abstract of a part of a thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Nebraska.

[2] Fischer, *Ber.*, **23**, 799 (1890).

[3] Nelson and Cretcher, THIS JOURNAL, **52**, 403 (1930).

[4] Fischer, *Ber.*, **24**, 3622, 3629 (1891).

[5] Cretcher, THIS JOURNAL, **49**, 478 (1927); **54**, 1590 (1932).

[6] Nef, *Ann.*, **357**, 276 (1907).

[7] Jensen and Upson, THIS JOURNAL, **47**, 3019 (1925).

[8] Nef, *Ann.*, **357**, 281 (1907).

[9] Anderson, *Am. Chem. J.*, **42**, 402 (1909).

[10] Jensen and Upson, THIS JOURNAL, **47**, 3024 (1925).