[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY
OF THE UNIVERSITY OF CHICAGO]

REACTIONS OF ATOMS AND FREE RADICALS IN SOLUTION. XIV. ADDITION OF POLYHALOMETHANES TO BUTADIENE SULFONE

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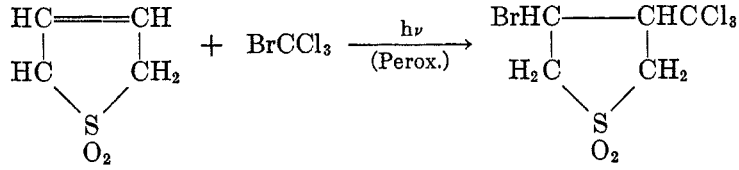
For some time the additions of polyhalomethanes to simple (1) and cyclic (2) olefins have been studied in this laboratory. The present paper deals with the additions of polyhalomethanes to an unsaturated heterocyclic compound, namely, butadiene sulfone (2,5-dihydrothiophene 1-dioxide).

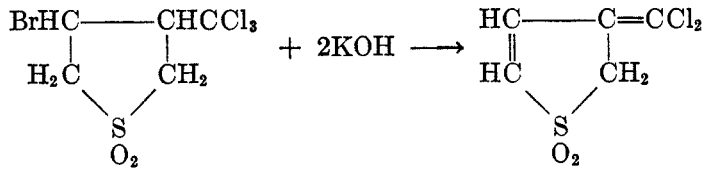
In the presence of light or peroxides (preferably diacyl peroxides) bromotrichloromethane reacts additively with butadiene sulfone to give 3-bromo-4-trichloromethyltetrahydrothiophene 1-dioxide (I),



I

as well as some sulfur dioxide and an oil containing no sulfur. Since there is no butadiene among the reaction products, the oil is probably a mixture of the 1,4 and 1,2 addition products of bromotrichloromethane to butadiene.[1]

Compound I is a crystalline material which melts at 141–142° (uncorr.). When it is treated in alcoholic solution with potassium hydroxide, two equivalents of base are consumed, and Compound II is formed.

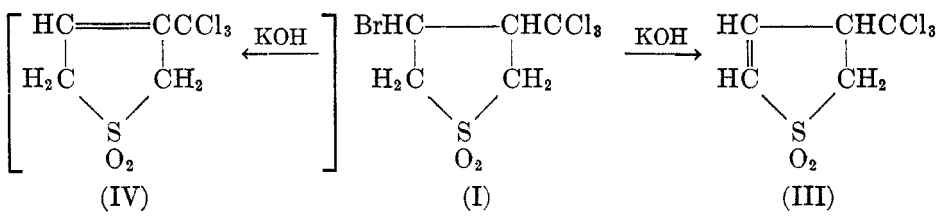


I II

The structure assigned to Compound II is in agreement with its analysis, molecular weight, and absorption spectrum.

When Compound I is treated with less than two equivalents of base, the product is a mixture containing some unchanged material and some Compound II. Probably the first step in the reaction is the removal of the hydrogen bromide to give Compound III; there follows a rapid reaction in which hydrogen chloride is eliminated to give Compound II.

[1] The compounds formed by the addition of bromotrichloromethane to butadiene have been carefully investigated (Kharasch and Nudenberg, unpublished work). Both the 1,2 (15–20%) and 1,4 (80–85%) adducts have been isolated.



The fact that, when I is treated with alkali, III, and not IV, is the compound first formed is of considerable theoretical interest. This subject will be discussed in a future publication dealing with dehydrohalogenation of the adducts of bromotrichloromethane and unsaturated cyclic hydrocarbons (3).

When carbon tetrachloride (instead of bromotrichloromethane) is heated (110°) with butadiene sulfone in an autoclave in the presence of a diacyl peroxide, the products obtained are similar to the ones already described. After six hours heating, 12% of a sulfur-free adduct, (presumably a mixture of 1,1,1,5-tetrachloropentene-2 and 1,1,1,3-tetrachloropentene-1)[1] is obtained. There is also 10% of an adduct of carbon tetrachloride to butadiene sulfone. That the structure of this adduct is similar to that of Compound I is shown by its ready conversion to Compound II by treatment with two equivalents of alcoholic potassium hydroxide. The product thus obtained does not depress the melting point of Compound II prepared from Compound I.

EXPERIMENTAL PART

Reagents. Butadiene sulfone (m.p. 65–66.5°) was prepared from butadiene and sulfur dioxide (4). Bromotrichloromethane was distilled at reduced pressure, and the fraction boiling at 42–43.6°/92 mm., $n_D^{19.2}$ 1.5060, was used.

The photochemical reaction of bromotrichloromethane with butadiene sulfone: the preparation of 3-bromo-4-trichloromethyltetrahydrothiophene 1-dioxide. A suspension of butadiene sulfone (11.8 g., 0.1 mole) in bromotrichloromethane (297.5 g., 1.5 moles) was irradiated by a mercury vapor-neon fluorescent coil in a reaction vessel equipped with a reflux condenser. A slow stream of nitrogen was passed through the reaction mixture. The top of the reflux condenser was connected to a bottle containing sodium hydroxide solution and a trap cooled at −78°. In thirty minutes the temperature of the reaction mixture rose to 70° and the butadiene sulfone dissolved. The solution was irradiated at that temperature for thirteen hours and then cooled. The crystalline material (*A*) which separated was collected on a filter and washed with 20 cc. of ice-cold bromotrichloromethane. After overnight drying in a desiccator, the material, (12.5 g.; 40% yield), melted at 139–140°. Upon crystallization from ligroin (65–70°), the compound melted at 141–142°.

Anal. Calc'd for $C_5H_6BrCl_3O_2S$: C, 18.98; H, 1.91; S, 10.13; Ag equiv., 79.11.
Found: C, 18.87; H, 2.03; S, 9.84; Ag equiv., 79.26.

The filtrate from *A* was concentrated to a volume of 40 cc. After cooling, large, glassy crystals (*B*) separated: unchanged butadiene sulfone (1.1 g.; m.p. 65–66°).

The filtrate from *B* was concentrated under reduced pressure until all the bromotrichloromethane had been removed. The residue was dissolved in ether and cooled. The precipitate (1.8 g., m.p. 53–118°), (*C*), was crystallized from 95% ethanol and yielded 0.77 g. of material, m.p. 81–130°, (*D*).

The ethanol filtrate from *D* was concentrated to dryness, and the residue was triturated with ether. The solid which separated, 0.41 g., m.p. 65–66.5°, (*E*) proved to be a further amount of unchanged butadiene sulfone.

The ethereal mother liquor from *C* was concentrated until only an oil remained. On distillation, a fraction, 4.95 g., b.p. 62–105°/0.8 mm., (*F*), was obtained. Decomposition was observed during the distillation. After overnight standing, this oil deposited large crystals, which were washed with a small amount of cold ether. The crystalline solid was butadiene sulfone, 0.94 g., m.p. 63.5–65.5°, (G). Thus, the total amount of unchanged sulfone amounted to 2.4 g. or 20%.

From the −78° trap connected to the distillation apparatus during the distillation of the oil, a small amount of white crystals, (*H*), of camphor-like odor was recovered. These sublimed at room temperature, and melted with sublimation in a sealed tube at 182–186°. The melting point of a mixture with an authentic sample of hexachloroethane showed no depression.

The sodium hydroxide solution was oxidized by addition of an excess of bromine water. After acidification, the excess bromine was removed. The solution was treated with an excess of barium chloride solution, and the insoluble sulfate was collected and ignited. The barium sulfate collected corresponded to 0.74 g. of sulfur dioxide, or 1.37 g. of butadiene sulfone.

No butadiene was found in the cold trap.

The peroxide-induced addition of bromotrichloromethane to butadiene sulfone: the preparation of 3-bromo-4-trichloromethyltetrahydrothiophene 1-dioxide. Butadiene sulfone (35.4 g., 0.3 mole) was added to bromotrichloromethane (268 g.) and the temperature raised to 80°. At that temperature, the sulfone was completely dissolved. A reflux condenser was attached to the reaction flask, and to the top of the condenser was connected a vessel, containing 1 *N* sodium hydroxide solution, and a trap cooled to −78°. A solution of acetyl peroxide (3.4 g.) in bromotrichloromethane (16 cc.) was added in five portions at thirty-minute intervals while the temperature was maintained at 80–85°. After all the peroxide had been added the solution was maintained for two hours at 85–88°. When the reaction mixture was cooled to 0°, a crystalline solid separated. This precipitate was washed with a small amount of cold bromotrichloromethane. The practically pure crystals proved to be 3-bromo-4-trichloromethyltetrahydrothiophene 1-dioxide (58.5 g., m.p. 138.5–140°, 61.7% yield).

The sodium hydroxide solution was treated with bromine water, and then with barium chloride solution. The weight of barium sulfate which separated corresponded to 1.98 g. of sulfur dioxide, or 3.6 g. of butadiene sulfone.

The bromotrichloromethane mother liquor was concentrated to 40 cc. and cooled overnight at 0°. The solid which crystallized was washed with 5 cc. of ice-cold bromotrichloromethane. The material, slightly impure butadiene sulfone (*K*), weighed 3.6 g. and had the melting point 57–59°.

The filtrate from *K* was concentrated under reduced pressure until all the bromotrichloromethane had been removed. The residue was triturated with 20 cc. of ether, and the solid which separated was washed with a small amount of ether. In this manner, a further amount of impure butadiene sulfone (2.6 g., m.p. 52–57°), (*L*), was obtained.

The ether filtrate from *L* was washed with water to remove the last traces of unchanged sulfone, and was dried over sodium sulfate. The ether was then removed, and the oily residue was distilled in vacuum. Three fractions were collected: (a) 3.0 g., b.p. 50–76°/0.4 mm., n_D^{24} 1.528; (b) 0.5 g., b.p. 76–100°/0.4 mm., n_D^{24} 1.535; (c) 4.0 g., b.p. 100–127°/0.35 mm., n_D^{24} 1.560. These three fractions did not decolorize bromine-carbon tetrachloride solution, but did decolorize potassium permanganate solution. They contained halogen, and did not contain sulfur.[1]

The material caught in the cold trap was warmed, and the escaping vapor was allowed to pass into a 5% solution of bromine in carbon tetrachloride. No precipitate of butadiene tetrabromide was obtained, nor was there any solid residue when the whole mixture was evaporated to dryness.

The reaction of the 1:1 addition compound of bromotrichloromethane and butadiene sulfone with potassium hydroxide: the preparation of 3-dichloromethylene-2,3-dihydrothiophene

1-dioxide. A portion of the bromotrichloromethane-butadiene sulfone addition product (2.75 g.) was dissolved in absolute alcohol (100 cc.), two drops of phenolphthalein solution was added, and the resulting solution was titrated with 0.45 *N* ethanolic potassium hydroxide until the appearance of a permanent pink color; 38.75 cc. of the potassium hydroxide solution was required (calculated for two equivalents of hydrohalogen acids, 38.66 cc.). A white solid (a mixture of KBr and KCl) separated and was washed with cold ethanol. The filtrate was concentrated to a volume of 10 cc. When the solution was cooled to 5°, a crystalline solid precipitated. This was washed with cold ethanol and dried in a desiccator overnight (1.45 g., 84% yield; m.p. 110–111.5°). The melting point of this material was not altered by crystallization from ether.

Anal. Calc'd for $C_5H_4Cl_2O_2S$: Cl, 35.63; mol. wt., 199.
Found: Cl, 35.04; mol. wt., 203.

The dichloro compound did not decolorize bromine, but did decolorize potassium permanganate solution very rapidly; it gave no precipitate with boiling alcoholic silver nitrate solution.

When the bromotrichloromethane-butadiene sulfone adduct was treated with one molecular equivalent of ethanolic potassium hydroxide, about 25% of unchanged material was recovered. Upon concentration of the solution, a material which melted at 89–97° was obtained (50%, by weight, of the adduct used). The melting point of this material was not changed by successive crystallizations. It is probably a mixture of butadiene-sulfone bromotrichloromethane adduct, and Compound II.

The reaction of butadiene sulfone with carbon tetrachloride in the presence of benzoyl peroxide in a steel autoclave. A suspension containing butadiene sulfone (35.4 g., 0.3 mole), carbon tetrachloride (185 g., 1.2 moles), benzoyl peroxide (0.6 g.) was heated for six hours at 110° in a steel autoclave. When this temperature was first attained, the pressure within the autoclave was 101 lbs./sq. in. The apparatus was allowed to cool to room temperature, and the excess pressure was released. The odor of sulfur dioxide was observed.

The dark reaction mixture was subjected to steam distillation. The lower organic layer of the distillate was separated, and the upper aqueous layer was extracted with 50 cc. of carbon tetrachloride. The combined organic extracts were dried over sodium sulfate, and the excess solvent was removed at atmospheric pressure. The residue was distilled in a vacuum, and the fraction (9.0 g.) boiling at 126–148°/57 mm. was collected. A redistillation of this material gave a fraction (7.2 g.; 12% yield) which boiled at 76–79°/5 mm., 127–129°/60 mm.; n_D^{20} 1.5060.

The residue which remained from the steam distillation, together with the water which had condensed during the steam distillation, was brought to a boil and filtered. On cooling, the filtrate deposited crystals, 1.66 g., m.p. 125–126°. Upon crystallization from methanol, the compound melted at 126.5–127.5°. This material gave strong positive tests for sulfur and chlorine.

A second quantity of crystals was obtained by extracting the residue from the dark reaction mixture with more boiling water. The filtered aqueous solution gave crystals, 0.8 g., m.p. 120–125°.

A third amount of material was obtained by powdering the remaining residue and shaking the dark powder with 200 cc. methanol at room temperature. The mixture was filtered, and the methanolic filtrate was concentrated to a small volume. After cooling to 0°, light brown crystals (6.2 g., m.p. 118.5–123°) separated. The material was dissolved in ether and boiled after the addition of activated carbon. From the ether filtrate, upon concentration, a white crystalline solid which melted at 125.5–127° was obtained. This material did not depress the melting point of the material previously isolated. The total weight of this substance was 8.7 g.

This crystalline material was shown to be an addition product of one mole of carbon tetrachloride to one mole of butadiene sulfone by the following experiment.

The reaction of the carbon tetrachloride-butadiene sulfone addition product with ethanolic potassium hydroxide. A portion of the solid product obtained in the above reaction (0.42

g., m.p. 126.5–127.5°) was dissolved in ethanol (50 cc.), two drops of phenolphthalein solution was added, and the solution was titrated with 0.446 *N* ethanolic potassium hydroxide; 6.92 cc. (0.174 g. potassium hydroxide) was required (calculated for two equivalents of hydrogen chloride, 0.173 g.). The ethanol was removed under vacuum, and the residue was dissolved in ether and filtered. The ether filtrate was concentrated to 2 cc. On overnight standing, crystals separated, which were washed with a little ice-cold ether and dried. White crystals melting at 110–111° were thus obtained. This material did not depress the melting point of the compound formed by the action of two equivalents of potassium

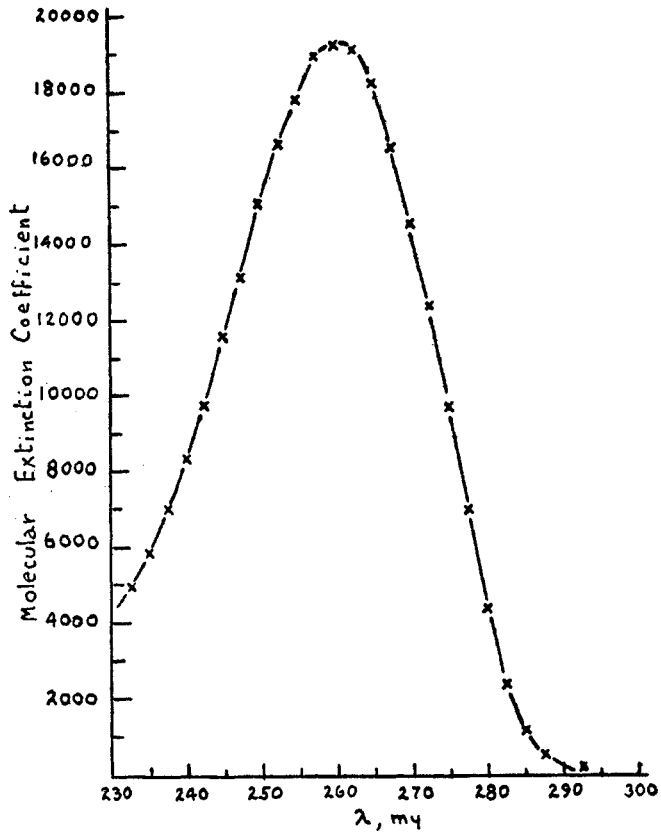


FIGURE 1. ABSORPTION SPECTRUM OF COMPOUND II IN ISOPROPANOL

hydroxide with one equivalent of 3-bromo-4-trichloromethyltetrahydrothiophene 1-dioxide (Compound II).

Absorption spectra. The spectra were determined with a Beckman quartz spectrophotometer, density readings being made at 5-mμ intervals, except in the region of a maximum where the readings were made at 1-mμ intervals.

The solvent used was 99% isopropanol (Carbide and Carbon). The concentration of the 3-dichloromethylene-2,3-dihydrothiophene 1-dioxide was 5.36 mg. per liter; that of the butadiene sulfone was 6390 mg. per liter, and that of the 3-bromo-4-trichloromethyltetrahydrothiophene 1-dioxide was 390 mg. per liter.

The absorption spectra of butadiene sulfone and 3-bromo-4-trichloromethyltetrahydrothiophene 1-dioxide are not given in Figure 1 since their absorption in the range from 2300

Å to 3000 Å is almost negligible. Butadiene sulfone gave a molecular extinction coefficient of 3.7 at 2300 Å, and its absorption dropped to a molecular extinction coefficient of 0.19 at 3000 Å. 3-Bromo-4-trichloromethyltetrahydrothiophene 1-dioxide showed a gradual fall in molecular extinction coefficient from 135 at 2300 Å to 6 at 3000 Å.

SUMMARY

1. The peroxide-induced and photochemical reactions of bromotrichloromethane with butadiene sulfone yield a one-to-one addition product, namely, 3-bromo-4-trichloromethyltetrahydrothiophene 1-dioxide.

2. The peroxide-induced reaction of carbon tetrachloride with butadiene sulfone yields a similar adduct, namely, 3-chloro-4-trichloromethyltetrahydrothiophene 1-dioxide.

3. The 3-halo-4-trichloromethyltetrahydrothiophene 1-dioxides, when treated with two molecular equivalents of alcoholic potassium hydroxide, yield 3-dichloromethylene-2,3-dihydrothiophene 1-dioxide.

4. A free-radical chain reaction is postulated to account for formation of the adducts from butadiene sulfone and polyhalomethanes.

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