product was obtained, but Werner failed to identify the latter. We have duplicated this work, finding the melting point of S-benzylthiourea as 94° on recrystallization from a mixture of benzene and petroleum ether. Several recrystallizations from dilute ethanol produced the 70–71° product, which we have characterized as benzyl disulfide.

Experimental Part

Electrolysis of Aqueous S-Aralkylthiuronium Chloride Solutions.—A 5–10% aqueous solution (25 ml.) of S-benzylthiuronium chloride was electrolyzed in a cell containing platinum electrodes (1 × 4 cm.) one centimeter apart. The initial current was 0.2–0.6 amp. at *ca.* 10 volts. At the outset, the cathode became covered with the fluffy product, trapping bubbles of hydrogen. The product could be removed by scraping the electrode or, better, by momentarily reversing the polarity. The maximum yield of product was 0.06–0.08 g. before its formation was stopped by the acidity produced simultaneously. The crude product had m. p. 92.5–93°. This was recrystallized from benzene and petroleum ether, decolorizing with Norit and keeping the temperature below 60°. The pure product had m. p. 94° dec., and showed no mixed m. p. depression and an identical absorption spectrum with the S-benzylthiourea below.

When the electrolyte solution was acidified prior to electrolysis, no cathode product was formed.

S-1-Naphthylmethylthiuronium chloride[3] in 1% aqueous solution gave crude S-1-naphthylmethylthiourea, m. p. 100° dec., when treated as above. On Norit treatment and recrystallization from a mixture of benzene and petroleum ether the m. p. was raised to 107° dec., unchanged when admixed with the free base described below.

S-Aralkylthioureas.—Werner[1] recommends the addition of one equivalent of dilute alkali to an aqueous solution of S-benzylthiuronium chloride for preparing S-benzylthiourea. We have had better results by adding dropwise just sufficient 30% sodium hydroxide solution to a 5–10% solution of the salt to form a thick slurry. This is filtered, and the filtrate similarly treated, until no more solid is formed. The water-rinsed, air-dried product had m. p. 92.5° dec., and showed a mixed m. p. of 93° dec. with the corresponding electrolytically deposited product above.

One gram of S-1-naphthylmethylthiuronium chloride in water (75 ml.) was treated with 30% sodium hydroxide solution as before. The total yield of crude, dried product, m. p. 104–105° dec., was 0.72 g. (84%). On recrystallization as before the m. p. was 108° dec.

Anal. Calcd. for $C_{12}H_{12}N_2S$: N, 12.98; S, 14.80. Found: N, 13.27; S, 14.97.

On melting, S-benzylthiourea rapidly resolidifies and remelts at *ca.* 190°. When S-benzylthiourea was heated at 115° for 15 minutes, it partially melted and small amounts of ammonia were evolved. The residue, smelling strongly of benzyl mercaptan, was recrystallized twice, with Norit treatment, from a mixture of benzene and methanol. The sulfur-free product had m. p. 207.5–208° and showed no mixed m. p. depression with an authentic sample of dicyandiamide of m. p. 209°. These results accord with those of Bernthsen and Klinger,[2] reported with no supporting experimental data.

When S-benzylthiourea was recrystallized four times from dilute ethanol after the method of Werner,[1] the product consisted of splendid needles, m. p. 70–71°. These showed no mixed m. p. depression and an identical absorption spectrum with an authentic sample of benzyl disulfide, m. p. 70–71°, prepared by the convenient method of Märker.[4]

Electrode Gases.—A solution of S-benzylthiuronium chloride was electrolyzed as before while inverting a water-filled tube over the cathode; 5.0 ml. of gas resulted after 5 minutes. Exactly the same procedure was employed at the anode, 2.6 ml. of gas resulting in the same length of time. When these gases were mixed and an electric spark passed through them, explosion resulted. These quantities and results are in accord with the liberation of hydrogen and oxygen at the electrodes.

Absorption Spectra.—The spectra in Fig. 1 were obtained with a Beckman model DU spectrophotometer, using 95% ethanol as solvent and making observations every 5 mμ.

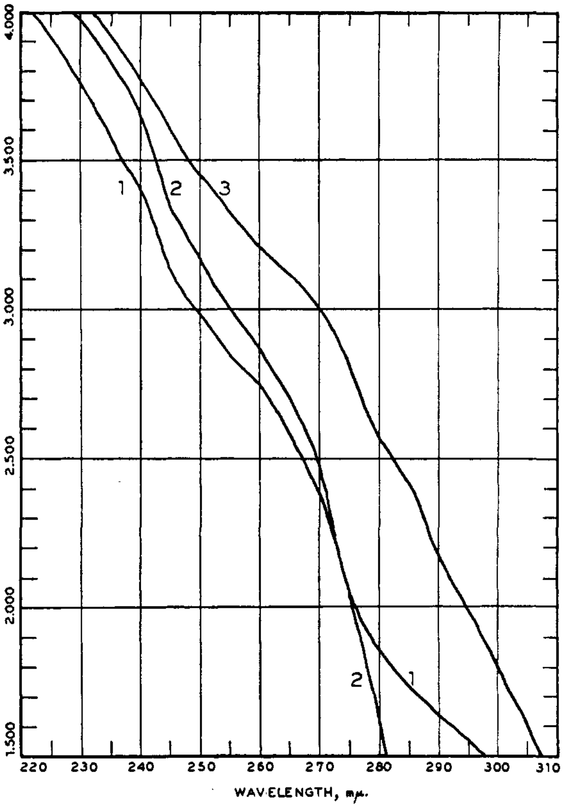

Fig. 1.—Absorption spectra: 1, S-benzylthiourea; 2, S-benzylthiuronium chloride; 3, benzyl disulfide.

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[3] W. A. Bonner, THIS JOURNAL, **70**, 3508 (1948).

[4] C. Märker, *Ann.*, **140**, 86 (1866).

The Exchange Reaction between Sulfur and Dibenzothiophene-5-dioxide

BY RAYMOND R. BROWN, SAM KIRKWOOD, LÉO MARION, STANLEY NALDRETT, ROBERT K. BROWN AND REUBEN B. SANDIN

Cullinane and Davies[1] have reported the conversion of dibenzothiophene-5-dioxide (I) to dibenzothiophene (II) by means of sulfur. The same reaction was carried out independently by Gilman and Jacoby[2] who obtained a 54% yield of recrystallized II from 5 g. (0.023 mole) of the sulfone and 0.9 g. (0.028 g. atom) of sulfur. This reaction is of considerable theoretical and preparative interest, and in view of this we have investigated the reaction between dibenzothiophene-5-dioxide and radiosulfur.

There are two possible reaction mechanisms: (1) sulfur removes oxygen atoms from the sulfone group, (2) sulfur displaces the sulfone group as sulfur dioxide. The relative stability of sulfones toward reducing agents makes the first reaction mechanism highly improbable. Moreover, it has been shown that when dibenzothiophene-5-dioxide is heated with tellurium the products are sulfur

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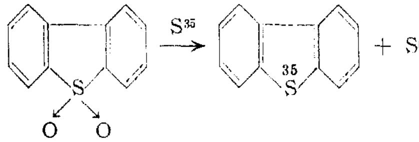
[1] N. M. Cullinane and C. G. Davies, *Rec. trav. chim.*, **55**, 881 (1936).

[2] H. Gilman and A. L. Jacoby, *J. Org. Chem.*, **3**, 108 (1939).

dioxide and diphenylene telluride.[3] Consequently it seemed to us that the second reaction, which is an exchange reaction, was the more likely. A rigorous method for establishing the mechanism was achieved by using radiosulfur. We now feel that it is highly probable that the replacement of the group $-\underset{\substack{\swarrow\ \searrow\\ O\quad O}}{S}-$ by sulfur is a direct one and is mainly



I II

This is in view of the fact that the sulfur dioxide and a small amount of hydrogen sulfide, which were both recovered as barium sulfate and counted as such, showed a radioactivity which was less than 4% of the activity of the original S^{35} containing barium sulfate. Moreover, the resulting dibenzothiophene was active and so this compound has become a useful starting material for the preparation of radiosulfur-containing carcinogenic compounds such as 3-acetaminodibenzothiophene (III).[4,5]

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Experimental

Radioactive barium sulfate[6] (0.2076 g.) with a specific activity of 47.6 × 10^5 counts per minute per gram of sulfur was converted to sodium sulfide according to the detailed procedure of Wood, Rachele, Stevens, Carpenter and du Vigneaud[7] who have prepared several mustard-type vesicants containing radiosulfur. Non-isotopic sodium sulfide (0.2645 g.) was added as carrier and the reduction to sulfur was carried out according to the directions of Wood, *et al.*[7] The sulfur (49.5 × 10^4 counts per minute per gram) was dissolved in *m*-xylene which was evaporated and replaced by carbon bisulfide. This solution was transferred to a 15-ml. exchange reaction flask which contained 2.57 g. of dibenzothiophene-5-dioxide. After the carbon bisulfide was evaporated the flask was heated in a potassium nitrate, sodium nitrite salt-bath. A dry inert atmosphere was supplied to the reaction flask by means of a nitrogen-filled gas holder. Nitrogen was also used to sweep the evolved sulfur dioxide and hydrogen sulfide through 3 ml. of a solution of 0.1 *M* zinc acetate and 0.2 *M* acetic acid contained in each of two bubbler tubes and through 3 ml. of 2 *N* NaOH contained in a third bubbler tube. The exchange reaction was carried out by heating for 2 hours at 320–330°, 30 minutes at 330–340°, 30 minutes at 360°, and finally for 15 minutes at 370–390°. The reaction mixture was steam distilled and the distillate was extracted with ether. After drying with anhydrous sodium sulfate and removal of ether, the residue was twice distilled under reduced pressure and crystallized once from ethanol. This afforded 0.2446 g. (31%) of dibenzothiophene, m.p. 98–99°; specific activity, 49.0 × 10^4 counts per minute per gram of sulfur. The dibenzothiophene was again twice distilled under reduced pressure and crystallized from ethanol. The activity of this material was 48.4 × 10^4 counts per minute per gram of sulfur. The sulfide precipitate from the first two bubbler tubes was centrifuged, oxidized to sulfate and counted as barium sulfate. The activity was less than 3% of the original barium sulfate. The centrifugate from the sulfide precipitate was combined with the material in the third bubbler tube, the sulfur oxidized to sulfate and counted as barium sulfate. The activity was less than 4% of the original barium sulfate.

Determination of Radioactivity.—All determinations were made with a windowless counter (Mark 9, Model 1, Nucleometer, purchased from the Radiation Counter Laboratories, Chicago, Illinois).

The gases collected from the exchange reaction were oxidized to sulfate and precipitated as barium sulfate. The precipitate was centrifuged, transferred in alcohol suspension to counting trays and counted as an infinitely thick layer. The activities of the dibenzothiophene and its derivatives were determined by counting infinitely thick layers of the pure crystalline substances. The same geometry was used in all measurements and a comparison was made with a reference standard. Corrections for self-absorption were applied.[8]

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(3) N. M. Cullinane, A. G. Rees and C. A. J. Plummer, *J. Chem. Soc.*, 151 (1939).

(4) J. A. Miller, E. C. Miller, R. B. Sandin and R. K. Brown, *Cancer Research*, **9**, 504 (1949).

(5) The conversion of active II into sulfur-labeled III was carried out by the 4-step process outlined by R. K. Brown, R. Christiansen and R. B. Sandin, THIS JOURNAL, **70**, 1748 (1948). The over-all yield of pure III was about 50%. The complete synthesis was carefully worked out with non-radioactive materials before the work with active materials was carried out.

(6) Barium sulfate containing radiosulfur was kindly supplied by the National Research Council of Canada, Division of the Atomic Energy Project, Chalk River, Ontario, Canada.

(7) J. L. Wood, J. R. Rachele, C. M. Stevens, F. H. Carpenter and V. du Vigneaud, THIS JOURNAL, **70**, 2547 (1948).

(8) W. F. Libby, *Ind. Eng. Chem., Anal. Ed.*, **19**, 2–6 (1947).

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Chain Electrolytes.[1] II

BY VICTOR F. H. CHU AND RAYMOND M. FUOSS

In a previous communication,[2] long chain polyelectrolytes were described in which nitrogen atoms of the chain were simultaneously the cationic sites; these were, however, also polyesters and hydrolyzed at an appreciable rate. In order to obtain stability in aqueous solution, compounds containing only carbon and nitrogen atoms in the chain seemed preferable. Searle[3] has described a number of such compounds obtained by the addition of α,ω-dibromides to α,ω-di-tertiary amines. Marvel and his co-workers[4] have shown that ω-halogenated amines undergo self-addition to give long chain quaternary salts when the nitrogen and the halogen atoms are separated by a sufficiently great distance to prevent cyclization. Both of these methods show promise of being very useful in the field of polyelectrolytes, because they permit the synthesis of compounds of known spacing between charges along the chain. The purpose of this note is to present some preliminary

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(1) Office of Naval Research, Project NR054-002; Paper No. 27.

(2) D. Edelson and R. M. Fuoss, THIS JOURNAL, **70**, 2832 (1948).

(3) N. E. Searle, U. S. 2,271,378, Jan. 27, 1942.

(4) M. R. Lehman, C. D. Thompson and C. S. Marvel, THIS JOURNAL, **55**, 1977 (1935).